AN ABSTRACT OF THE THESIS OF

Terry Lee Ramus for the degree of Doctor of Philosophy

in Chemistry presented on June 5, 1985.

Title: DETERMINATION OF CHLORINATED HYDROCARBONS BY RESPONSE FACTOR CALIBRATION

Abstract approved: Redacted for privacy

Lawrence C. Thomas

A new method is developed and evaluated in this thesis research for measuring analytes by chromatography in the absence of reference materials which contain the analytes of interest. The method is applied to determinations of chlorinated hydrocarbons, using gas chromatography and the Hall electrolytic conductivity detector (HECD). A chlorinated hydrocarbon, different from analytes of interest and containing known organochlorine equivalents, is added to samples prior to analysis and this compound is referred to as the response standard. The response standard and analytes are both reduced to HCl, the simple measured species, and the response standard is used to measure the HECD response factor to organically bound chlorine. A response ratio is defined to be the analyte peak area divided by the response standard peak area, both measured during a single chromatogram. The response ratio, measured by GC-HECD, is found to be linearly related to analyte organochlorine equivalents for chlorinated hydrocarbons.

The generalized procedure for analyte determinations in the absence of identical analyte reference materials is labeled Response Factor Calibration (RFC). RFC methods produce the same simple measured species both from analytes of interest and the response standard, and subsequently measure the simple species.

Chlorinated hydrocarbons can be determined by RFC in organochlorine equivalents, since HCl is measured in the HECD. Analyte determinations can be expressed in analyte mass if certain stoichiometric information is available. However, complete analyte identification is not required for analyte determination with RFC. RFC with GC-HECD were applied to determinations of hexachlorocyclopentadiene photolysis products. RFC was also used to determine selected PCB isomers in Aroclor mixtures with an adapted capillary-GC-HECD system developed in this thesis research.

Criteria are provided for using the HECD with RFC. Efficiencies for organochlorine reduction to HCl were measured for several chlorinated hydrocarbons to guide selection of HECD reactor temperatures. HECD reactor products were monitored by mass spectrometry for these temperature dependence studies using a specialized GC-HECD-reactor-MS system developed in this research.

Flow conditions for the HECD were evaluated in a factorial experiment. A polynomial model was used to describe a response surface and to estimate the relationship between the flow factors and the HECD response. Carrier gas flow through the HECD was found to significantly affect the HECD response. A special constant mass-flow system was employed to provide constant HECD flows, even during temperature programmed analyses.

DETERMINATION OF CHLORINATED HYDROCARBONS BY RESPONSE FACTOR CALIBRATION

by

Terry Lee Ramus

A THESIS

submitted to

Oregon State University

in partial fulfillment of

the requirements for the

degree of

Doctor of Philosophy

Completed June 5, 1985

Commencement June, 1986

APPROVED:

Redacted for privacy

Professor of Chemistry in charge of major

Redacted for privacy

Head of Department of Chemistry

Redacted for privacy

Dean of Graduate School

Date thesis is presented June 5, 1985

Typed by Patty Ramus for Terry Lee Ramus

ACKNOWLEDGMENTS

I have many individuals to thank for contributions toward my achievement of this goal:

My wife, Patty, for her love, affection and devotion. She has been patient, tolerant and supportive as I advanced and learned at universities, often sacrificing her own desires in order to expedite the achievement of my own goals.

My daughters, Erin and Jessica have been enjoyable and entertaining, and they forced further focusing of my efforts following their arrivals.

My father, mother and family for a strong commitment and constant support. They have always strived to instill the importance of self-reliance, the establishment of goals, endurance, and ethical achievement.

A special thanks to my father, Joseph Ramus, for sharing his knowledge with me as I learned the "C" programming language utilized in this thesis research.

Dr. Larry Thomas for guidance and contributions as my research advisor, and constant efforts toward acquainting and maturing me toward a future successful career.

The Chemistry Department ~~facility~~ faculty at Oregon State University for guidance, instructional efforts and confidence in my abilities.

Partial funding was provided through the Tartar Fellowship Awards and the Bowerman Foundation.

CONTRIBUTION OF AUTHORS

Terry L. Ramus	Developed ideas; implemented experiments to test ideas; evaluated experimental results and developed conclusions; and presented results and conclusions in manuscript format.
Lawrence C. Thomas	Major Professor. Contributed many ideas, facilities, and a research environment.
Scott J. Hein	Section IIIa: contributed ideas and experience during mass spectrometry experiments.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

DETERMINATION OF CHLORINATED HYDROCARBONS BY RESPONSE FACTOR CALIBRATION

I. INTRODUCTION

Analytical Chemists devote much effort toward preparation and characterization of reliable reference materials, which are usually required in analytical procedures for analyte determinations. For example, several methods are routinely used for analyte determinations by chromatography when the analyte of interest can be obtained in a reference material (see Section II). However, methods for analyte determinations by gas chromatography are not well established if reliable reference materials, containing the analytes of interest, are unavailable. This research addresses determinations of chlorinated hydrocarbons by gas chromatography in the absence of such reference materials. The method developed for analyte determinations with the Hall Electrolytic Conductivity Detector (HECD), following chromatographic separation in the absence of reference materials, may be generalized. The method has been labeled herein as Response Factor Calibration (RFC).

Unavailability of an analyte reference material is often encountered in analyses of complex toxicologic or environmental samples. Reference materials may be unavailable when analytes have unknown identities, are labile under the experimental conditions, or require complicated synthetic procedures for reference material preparation. Furthermore, procedures used to identify the analyte and to synthesize or characterize a reference material may employ

specialized laboratory techniques. However, time and available resources often limit such extensive efforts toward preparing a reliable reference material.

Analyte response factors must be known in order to relate instrumental responses to analyte concentrations by conventional quantitative methods for chromatography. Analyte reference materials, if available, allow instrumental response factors to be measured directly. However in the absence of reference materials which contain the analytes of interest, response factors for the eluates are often assumed to be equivalent to measured response factors for a class of similar compounds. Thus, analyte concentrations are calculated from the assumed response factor without an identical analyte reference material. Consequently, these assumed instrumental response factors yield only concentration estimates, unless shown to be accurate. Moreover, if eluate identity is unknown, quantitative analyses are even less tractable. A method is developed in this thesis research for the determination of chlorinated hydrocarbons in the absence of identical reference materials for each analyte, and also for measurements of incompletely identified analytes. It is based on fundamental principles and supported by experimental results.

Response factor calibration procedures developed herein allow for analyte determinations by chromatography in the absence of reference compounds identical to each analyte of interest. Response factor calibration requires an unambiguous response _vs_. analyte concentration relationship. Moreover, the response factors for the measured species must be independent of analyte origin.

These restrictions may be met if constant response factors can be obtained by reacting the analytes to form a common reaction product, or simple measurable species. The measured response for the simple species may then be related to analyte concentration via stoichiometry.

Assumptions about response factors are less restrictive in RFC since the same simple species is measured from different eluates. However, RFC requires reproducible and constant formation efficiencies of the simple species from analytes of interest. Consistent with this requirement, quantitative formation of HCl from organochlorine was confirmed for chlorinated hydrocarbons of interest using a GC-HECD-reactor-MS system developed for this work.

Additional information about the eluates is required to establish stoichiometric relationships, e.g. analyte molecular weight, the number of chlorines per molecule, or perhaps analyte identities. Supplemental GC-MS data may be used to establish the number of chlorines per analyte molecule or analyte molecular weight. This stoichiometric data allows for organochlorine determinations to be expressed in units other than organochlorine equivalents, such as grams of analyte per liter (see Section III).

RFC for gas chromatography and the Hall Electrolytic Conductivity Detector (HECD) is studied in this thesis research and applied to determinations of chlorinated hydrocarbons in the absence of identical analyte reference materials, and in the absence of complete analyte identification. Gas chromatographic separations were used to isolate chlorinated hydrocarbon analytes from a response standard and from other eluates present in a sample

matrix. The HECD forms HCl, the simple measured species from chlorinated hydrocarbons, in a high temperature catalytic reactor and measures HCl by conductometry in a differential conductance cell. Analyte organochlorine equivalent determinations, via HCl measurements, and stoichiometric relationships allow for chlorinated hydrocarbon determinations.

RFC procedures require the inclusion of a response standard which is added to the sample solution prior to chromatographic separation, e.g., a chlorinated hydrocarbon of known concentration. Procedurally, this is similar to the addition of an internal standard for chromatographic determinations. However, RFC is different than internal standard methods for chromatography. The added response standard contains a known amount of organochlorine and is used to establish the response factor for the simple measured species from all analytes for each chromatogram. Thus, separate elutions of reference compounds identical to each analyte are not required.

Applications of chlorinated hydrocarbon determinations in the absence of reference materials by RFC are presented in Sections III and VIII. Unidentified photolysis products of hexachlorocyclopentadiene (HCCPD) are quantitatively measured without identical reference materials. Thus, the parent compound and unidentified product concentrations are easily monitored during the photolysis experiments, yielding kinetics information. Also, polychlorinated biphenyl (PCB) isomers are determined without identical reference materials for each PCB eluate using RFC.

II. HISTORICAL

Overview of Reference Materials for GC

Reference materials make comparisons possible between different measured quantities. A reference material (RM) is defined by the International Organization for Standardization (IOS) as a material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus or for the verification of a measurement method [1, 2]. Reference materials accompanied by a certificate stating the property values of concern, issued by a technically competent organization, are called certified reference materials (CRM).

The U.S. National Bureau of Standards (NBS) categorizes Reference Materials as follows:

A. Standard Reference Material (SRM): a reference material having given properties with numerically assessed values, within given tolerances, certified by an appropriate technical body [3].

   1. Standard Calibration Material (SCM): a certified material with defined composition and physical structure used for the calibration of an apparatus intended for physico-chemical measurements and as such as references for physico-chemical measurements [3]. SCMs are a subset of SRMs.

B. Uncertified Reference Materials.

1. Calibration Material (CM): a recommended material with defined composition and physical structure used for the calibration of an apparatus intended for physico-chemical measurements and as such as references for physico-chemical measurements [3].
2. Test Material (TM): materials with stated composition and physical structure of lower accuracy than CMs used for physico-chemical measurements [3]. TMs are not officially recommended. Fewer experimental techniques are employed to established the composition and physical structure of TMs than CMs.

Reference materials used in gas chromatography may be SCMs, CMs or TMs as defined by NBS. TMs are routinely used in gas chromatography for analyte determinations by a single procedure within a single laboratory. Test materials may be purchased on the open market or prepared by the laboratory. CMs or SCMs are periodically employed in gas chromatography to establish the degree of experimental compatibility between different instruments, procedures or laboratories. Knowing the degree of experimental compatibility may allow for comparisons of results arising from different sets of measurements.

This thesis manuscript usually refers to SCMs, CMs and TMs for gas chromatography by the more general term, reference material. GC reference materials may be either test or calibration materials. Herein an analyte reference material (ARM) specifies a reference material which contains the analyte of interest and is employed for determinations of the analyte of interest. An analyte reference

compound is specified as the particular analyte of interest contained at known amount in the analyte reference material.

Reference materials may be homogeneous materials of known composition, perhaps substances prepared at high purity. Composition and purity should be well defined, controlled, and checked by reliable and accepted analytical procedures [3]. The concentrations of other compounds, including impurities, within the reference material should also be known. The composition of reference materials should be stable under storage conditions for at least two years and stable during experimental procedures [3].

Satisfying the requirements for reference material preparation can be difficult and painstaking. The requirements are not always met in routine GC work. Often analytes of interest for gas chromatography are complicated in structure, difficult to synthesize and purify, and may be unstable during storage and experimentation. The preparation of reference materials for such complex analytes in gas chromatography presents a challenging and formidable task.

A few certified reference materials for GC are available for purchase from governmental agencies such as the NBS or EPA, and occasionally from chemical suppliers or equipment manufacturers. However, most important analytes of interest remain without a source of certified reference materials. Moreover, TMs are not available for many analytes, especially if their identities are unknown. Therefore, methods which do not require RMs or TMs are needed if those important analytes are to be measured without reference materials.

Methods for Quantitative Analyses with GC

Methods for quantitative analyses in GC have been organized according to their requirements for analyte reference materials and analyte identification. Methods for analyte determination in GC can be divided into three categories. The first category, measurements which require identical reference materials, includes the External Standard, Internal Standard and Standard Addition methods. The second category, measurements in the absence of identical reference materials, includes response factor assumption, response factor calculation, and response factor calibration methods. The third category, measurements without analyte identification, includes RFC but does not yet contain many established GC methods. These organizational groupings are useful to the analyst selecting methods for analyte determination by chromatography.

Methods for analyte determinations by GC using analyte reference materials are well established. However, these methods require both complete analyte identification and acquisition of a reference material for each analyte of interest prior to determination. Quantitative analyses in gas chromatography use analyte reference materials to measure instrumental response factors for each analyte of interest. The response factor for the analyte reference compound, f_r, is equivalent to the instrumental response resulting from elution of that reference compound into the detector divided by the reference compound mass, M_r. Peak area, A_r, is typically the observed instrumental response and the response factor can be expressed accordingly [4],

$$f_r = \frac{A_r}{M_r} \quad (1)$$

f_r may vary with M_r, but is constant in linear systems. The response factor for an unknown amount of the same analyte, eluted from a sample, is assumed to equal f_r. Thus, f_r may be used to determine the unknown analyte mass, M_u, contained in a sample from the measured analyte peak area, A_u. However, in the absence of an analyte reference material the instrumental response factor cannot be measured directly and thus the unknown analyte mass cannot be determined using these methods.

Measurements Which Require Identical Reference Materials

Established methods for analyte determinations with gas chromatography require identical reference materials for each analyte of interest, which mandates analyte identification. The methods thus require a direct measurement of the instrumental response factor using an analyte reference material. Three methods for analyte determination using reference materials are External Standard Methods (ES), Internal Standard Methods (IS) and Standard Addition Methods (SA).

External Standard Method (ES). The external standard method compares the analyte peak area, $A_{u,2}$, from samples which contain an unknown analyte mass, $M_{u,2}$, to analyte peak areas, $A_{s,1}$,

obtained from standards which contain a known analyte mass, $M_{s,1}$ [5, 6]. Standard solutions are prepared from analyte reference materials and are used to measure the instrumental response factor for each analyte of interest. These standards are called external analyte standards and the identical eluates contained in both the sample and standard solutions must be evaluated during separate GC elutions, e.g. 1 and 2. Moreover, chromatographic conditions must be the same during both elutions for valid quantitative results [5]. The unknown analyte mass, $M_{u,2}$, can be calculated as,

$$M_{u,2} = \frac{M_{s,1}}{A_{s,1}} \cdot A_{u,2} \qquad (2)$$

and the instrumental response factor, f_{ES}, is

$$f_{ES} = \frac{A_{s,1}}{M_{s,1}} \qquad (3)$$

where
- M denotes mass
- A denotes peak area
- u indexes analyte at unknown concentration in sample solution
- s indexes analyte at known concentration in standard solution
- 1 indexes GC elution #1
- 2 indexes GC elution #2
- ES denotes external standard method

External standard methods require at least two separate GC elutions since the external analyte standard's response factor must be measured during a different elution than the analyte in the sample: they have identical retention times. Furthermore, external standard methods require that complete analyte identity be established so that an analyte reference material can be obtained.

External standard solutions are often prepared at several concentrations spanning a range which includes the unknown analyte concentrations, and a calibration curve is prepared. The calibration curve allows the relationship of instrumental response vs. analyte mass to be evaluated and used for calculations. The first derivative of the calibration curve represents the instrumental response factor for a particular analyte mass. However, for external standard methods the instrumental response factor must remain constant during quantitative measurements of both standards and unknowns, injection volumes must be precisely delivered, and the analyte peak must be completely resolved.

Internal Standard Method (IS). The internal standard method is a subset of the external standard method since an external analyte standard for each analyte is also used, similar to the ES method described above to directly measure instrumental response factors. However, a second standard, called an internal standard, is included for each GC elution [4, 5, 6]. The internal standard should have similar physical and chemical properties to the analyte of interest, and the internal standard should elute near the analyte peak [5]. Both the analyte of interest and the internal standard must be resolved, and the internal standard must not be present in the sample matrix.

Known masses of the internal standard are added to both analyte standard and sample solutions, usually to yield the same internal standard concentration, prior to chromatographic separation. The instrumental response factor for the analyte of interest is

measured relative to the response for the internal standard via elution of the analyte standard solution [5],

$$f_{IS} = \frac{A_{s,1}}{M_{s,1}} \cdot \frac{M_{i,1}}{A_{i,1}} \tag{4}$$

where
i indexes internal standard at known concentration in solutions
IS denotes internal standard method

Measurements from a subsequent elution of the sample analyte solution and the previously measured instrumental response factor, f_{IS}, allow calculation of the unknown analyte mass [5],

$$M_{u,2} = \frac{1}{f_{IS}} \cdot \frac{A_{u,2}}{A_{i,2}} \cdot M_{i,2} \tag{5}$$

The internal standard method compensates for variations due to imprecise injection volumes and interelution variations in response factors. The internal standard should be stable, nonreactive, nonvolatile, and of known composition.

Usually a series of analyte standard and sample solutions are used, all of which contain the same concentration of internal standard. Thus, the internal standard masses for the sample, $M_{i,2}$, and standard solutions, $M_{i,1}$, are equal, simplifying equation 5,

$$M_{u,2} = \frac{A_{i,1}}{A_{s,1}} \cdot \frac{A_{u,2}}{A_{i,2}} \cdot M_{s,1} \tag{6}$$

Calibration curves may be prepared for evaluation over a range of analyte standard concentrations, and used for quantitative

analyses. Similar to ES methods, internal standard methods require prior analyte identification, an available analyte reference material and at least two GC elutions. Moreover, a second reliable reference substance for the internal standard must also be selected, obtained, and properly added to solutions.

Standard Addition Method (SA). Standard addition methods in gas chromatography are similar to internal standard methods except for the origin of the analyte standard solution. Both internal standards and external analyte standards may be utilized [5]. The analyte sample solution, perhaps containing an internal standard, is separated during the first GC elution to yield peak area measurements, $A_{u,1}$ and $A_{i,1}$, for the analyte of unknown mass, $M_{u,1}$, and the internal standard, respectively. Next, a known mass of external analyte standard, $M_{s,2}$, is added to the previously measured sample matrix. A second GC elution yields peak area measurements, $A_{u+s,2}$ and $A_{i,2}$, for the total analyte and internal standard, respectively. If volume changes result in insignificant dilution, then the instrumental response factor, f_{SA}, can be expressed as,

$$f_{SA} = \left(\frac{A_{u+s}}{M_{s,2} + M_{u,1}} \right) \cdot \frac{M_{i,2}}{A_{i,2}} \qquad (7)$$

If the internal standard masses for GC elutions 1 and 2 are equivalent by experimental design, $M_{i,1} = M_{i,2}$. Thus, the unknown analyte mass, $M_{u,1}$, can be calculated [5],

$$M_{u,1} = \frac{M_{s,2}}{\left(\frac{A_{i,2}}{A_{u+s,2}} \cdot \frac{A_{u,1}}{A_{i,1}}\right) - 1} \qquad (8)$$

Requirements for both the IS and ES methods regarding resolution and selection of standards also apply to the standard addition method. The standard addition method, like ES and IS methods, requires analyte identification, analyte reference materials, at least two GC elutions, and reliable IS reference materials, if used.

Several sequential additions of the analyte standard to the sample solution, each followed by GC elution and measurement, can be used to produce a calibration curve [5]. Advantages of the standard addition method include compensation for some matrix effects, and a resolved sample component originally present in complicated sample matrices may be used as the internal standard [5].

Measurements in the Absence of Identical Reference Materials

Often analytes of interest have no available analyte reference materials, and therefore established gas chromatographic methods for analyte determination, IS, ES and SA methods, cannot be employed. Analyte reference materials may be unavailable due to unestablished or ambiguous analyte identification, analyte instability under experimental conditions, synthesis difficulties arising from complicated analyte structure, or unsuccessful analyte

purification from complicated mixtures. However, determinations of some analytes which do not have available reference materials may be important. For example, analytes of concern in environmental, toxicologic, and industrial process analyses often remain undetermined due to the absence of analyte reference materials.

Several gas chromatographic techniques have been used for analyses for which analyte reference materials are unavailable. The techniques include assuming response factor equivalency for similar compounds or response factor calculation based on additive functional group contributions to instrumental response. Response factor calibration is another alternative, and is the subject of this thesis research.

Assumptions for Response Factor Equivalency. Analysts may, usually based on experience, assume that the instrumental response factors for an analyte of interest and a different but available reference compound are equivalent. For example, in gas chromatography the flame ionization detector is sometimes assumed to respond linearly to the amount of analyte carbon. Similarly, a mass spectrometer might be assumed to respond linearly to the amount of analyte. Along these lines of thought, Tong and Karasek reported that FID response factors to carbon for 16 normal alkanes varied by 1.4% RDS and varied by 5.7% RSD for 22 polycyclic aromatic hydrocarbons [7, 8]. Likewise, Pearcy, Rowland, Mack and Coll observed the FID response factor to carbon for malonic acid derivatives to range within 6% [9]. These data support assumptions of response equivalency, but are based on approximate relationships and thereby

result in analyte estimations, and they should be implemented only when other approaches are not feasible. However, these assumptions are often used for routine analyses in analytical laboratories.

Response Factor Calculation. Instrumental response factors may be calculated for analytes in the absence of analyte reference materials from which to measure directly the actual response factor. Such estimations are empirically based since representative contributions by particular groups to analyte response factors are used for particular classes of compounds. Representative response factor adjustments may be used systematically for analyses, perhaps based upon empirically observed changes in the response factors for different analytes with branching or specified functional groups.

The flame ionization detector (FID) for gas chromatography is occasionally used with empirically based response factor calculations for analyte determination. For example, Perkins, Laramy and Lively used empirically measured effective carbon values to calculate detector response factors [10]. The FID was observed to respond linearly to the number of carbon atoms, N_C, for normal alkanes and linearly with the carbon number minus one-half for alcohols. Thus, the effective carbon number is N_C for normal alkanes and N_C-1/2 for alcohols [10]. Similarly, Edwards observed the effective carbon number for several steroids and carboxylic acids to be N_C-1/2N_O where N_O is the number of oxygen atoms [11].

FID response factor relationships are not always so straightforward. For example, Askew and Maduskar did not find a simple

correlation between FID response and carbon number for perfluoroalkanes [12], but Elliott observed the FID response factor for perfluorinated carboxylic acids to be approximately twice that for hydrocarbon carboxylic acids [13]. Thus, these empirical FID response factor relationships seem useful only for simple alkanes and oxygen containing hydrocarbons.

For GC-mass spectrometry, the relative total ionization cross-sections of molecules may be related to response factors, since the total ion current may be proportional to the total ionization cross-section and the analyte concentration [14]. Relative total ionization cross-sections for molecules have been shown to be additive from atomic total ionization cross-sections in mass spectrometry [14, 15]. However, other work suggests that the relationship is more complex than simple addition [16, 17]. Nevertheless, relative total ionization cross-sections for molecules have been used, based upon calculations from analyte molecular weight and molecular structure, and related to response factors in mass spectrometry [14, 18]. Fitch and Sauter reported that the average error in the prediction of relative total ionization cross-sections for 179 molecules was less than 5% [14]. The 179 molecules evaluated contained carbon, hydrogen, oxygen, fluorine, chlorine, bromine and iodine groups.

Webb and McCall utilized the Coulson conductivity detector with packed column GC to quantitate Aroclor peaks [19]. Detector area responses to a known mass of p,p'-DDE, molecular weights, and molar chlorine content were used to calculate the response factor for the Coulson detector to organochlorine. This calculated response factor

was used to determine Aroclor eluates from separate GC elutions. The determinations were stated to be based on an assumed linear relationship between the coulson detector response and analyte organochlorine. However, evidence for the coulson detector linearity to organochlorine was neither presented nor referenced.

Response Factor Calibration (RFC) Developed in This Thesis. Response factor calibration procedures developed in this thesis research allow for analyte determinations with gas chromatography in the absence of analyte reference materials [20, 21]. GC eluents are quantitatively reacted to yield a simple measurable species for detection. The instrumental response factor for the simple species is measured for a response standard of known mass which elutes from the GC and reacts quantitatively to yield the same simple measured species as the analyte of interest.

The response standard, a substance different than the analyte of interest, is obtained as an available reference material, and a known amount is added to each sample solution. The response standard and analyte of interest are delivered concurrently to the GC within the same injection, and they elute separately from the GC into the high temperature reactor to form quantitatively an identical simple measured species. Thus the known amount of response standard establishes the instrumental response factor for the simple species, allowing calculation of simple species equivalents for the analyte of interest. The simple species is therefore an indicator substance which is identical for both analyte and response standard eluates. Consequently, analyte determination is

achieved with RFC by using a response standard to measure the response factor for the simple species, instead of using individual analyte reference materials to measure each analyte's response factor.

The response factor for the simple species, f_{RFC}, is obtained from the measured peak area for the response standard, $A_{rs,1}$, of known simple species equivalents, $X_{rs,1}$,

$$f_{RFC} = \frac{A_{rs,1}}{X_{rs,1}} \tag{9}$$

where
- X denotes equivalents of the simple measured species
- rs indexes the response standard
- RFC indexes the response factor calibration method

The instrumental response factor for the simple species, f_{RFC}, can also be expressed in units of mass, using the response standard mass, $M_{rs,1}$,

$$f_{RFC} = \frac{A_{rs,1}}{\left(\frac{M_{rs,1} \cdot N_{rs}}{MW_{rs}}\right)} \tag{10}$$

where
- N denotes the number of simple species equivalents per mole of analyte
- MW denotes molecular weight

If the instrumental response factor remains constant during elution of both the analyte and the response standard, then the analyte can be determined from the measured analyte peak area, $A_{u,1}$, in units of simple species equivalents, $X_{u,1}$,

$$X_{u,1} = \frac{1}{f_{RFC}} \cdot A_{u,1} \qquad (11)$$

Alternatively, calculations may be made or in units of analyte moles if the number of simple species equivalents per mole, N_u, is known. Analyte mass, $M_{m,1}$, may be calculated if the molecular weight, MW_u, and N_u are known for the analyte.

$$M_{u,1} = \frac{1}{f_{RFC}} \cdot \frac{MW_u}{N_u} \cdot A_{u,1} \qquad (12)$$

RFC requires that the response standard and analyte of interest be resolved. The response standard must be well characterized and must not be present in the sample matrix. It is best if the response standard has physical and chemical properties similar to the analyte of interest and elutes near the analyte peak. A RFC calibration curve can be prepared as with the conventional methods for determination by GC. The calibration curve is the response ratio, $A_{u,1} / A_{rs,1}$, versus the simple species equivalents of the analyte, and 1/slope equals the simple species equivalents for the response standard.

RFC has several important advantages for analyte determinations, as compared to the conventional ES, IS and SA methods for GC. First, RFC does not require a reference material identical to each analyte since a standard analyte solution of known concentration is not required to measure the instrumental response factor for the analyte. Instead, the instrumental response factor for the simple species is measured using information arising from a

different, separately eluting compound, a response standard. Second, complete analyte identification prior to determination is not required in RFC. However, supplemental information can be employed to establish stoichiometric relationships, analyte molecular weight, and the absence of co-eluting interferents. Third, all information needed for analyte determination is available from each individual chromatogram. Thus, variations in the chromatographic conditions between elutions do not affect analyte determination by RFC.

Response factor calibration is developed and applied in this thesis research with GC and the Hall Electrolytic Conductivity Detector (HECD) for the determination of chlorinated hydrocarbons. Chlorinated analytes and a response standard elute from the GC enter the HECD. Organochlorine reacts to produce HCl, the simple measured species, in the high temperature catalytic reactor of the HECD. The HECD measures the simple species, HCl, in the differential conductivity cell.

A chlorinated response standard is added to sample solutions at known mass prior to chromatographic separation, and it is used to measure the HECD response factor for organochlorine. Supplemental GC-MS data may be included to establish the number of analyte organochlorine equivalents per mole of analyte and molecular weights. Thus, chlorinated hydrocarbons are determined in either units of organochlorine equivalents or analyte mass without analyte reference materials. Moreover, complete analyte identification is not required.

Classification of this new method for analyte determination, RFC, among the established techniques in gas chromatography, ES, IS and SA, can be ambiguous. If an "internal standard" is defined to be a compound added directly to the sample solution to aid in measurement, and an "external standard" is defined to be a compound used to evaluate response factors via solutions different than the sample solution, then the response standard for RFC would be categorized as an "internal standard." However, categorizing GC methods with these criteria would reveal the following: (a) the IS method and the SA method require both "internal" and "external standards," (b) the ES method uses only "external standards," and (c) RFC uses only "internal standards." These classifications may be interesting but are not particularly informative about the more important differences which are of interest to the analyst using gas chromatography.

For chromatography the following classification scheme is helpful and consistent with accepted laboratory practices. The ES, IS and SA methods in GC all use analyte standard solutions of known concentration, prepared from analyte reference materials, to measure the instrumental response factor. However, RFC uses reference compounds different from the analytes of interest, added to sample solutions, for response factor measurement. Moreover, RFC does not require separate analyte standard solutions prepared from analyte reference materials. These are important differences between RFC and conventional GC methods.

RFC also requires only a single elution, which is distinctly different than conventional ES, IS and SA methods. For RFC the

instrumental response factor is measured via the eluted response standard and then that response factor is used for analyte determinations within the same elution. On the other hand, for the IS method a second reference material must also be included in all solutions which is different from the analyte of interest, but the internal standard is used to relate at least two required elutions. In this thesis the added reference compound in RFC is defined as a response standard to distinguish it from other uses for added reference compounds, as in ES, IS and SA methods.

Measurements Without Prior Analyte Identification

The external standard method, internal standard method, and standard addition method for analyte determination in gas chromatography cannot be used when complete analyte identity is not established. If analyte identity is unknown, then choosing an identical analyte reference material is not feasible. Furthermore, using assumptions about response factor equivalency prior to analyte identification may be invalid, and response factor calculation procedurally requires analyte identification. However, response factor calibration can be used for quantitative measurements even in the absence of complete analyte identification. RFC determinations are most useful if previous experimentation has shown reproducible conversion of the analyte of interest to the simple measured species, and if interferents are shown not to be present, as described in Sections III and IV.

Determinations of Polychlorinated Biphenyls

Prior to 1977, polychlorinated biphenyls (PCB's) were widely used in the U.S. PCBs are very stable compounds, not easily hydrolysed by water, acid or alkali, and possess such thermal stability that they are used for fire-proofing [22]. Manufacturers produced similar chemicals by chlorinating biphenyls, terpenyls, and naphthalenes to yield complex mixtures of many compounds and isomers. The mixtures were marketed under trade names such as Arochlor, Phenochlor and Chlophen [22]. These products contained a myriad of chemical compounds. The PCB products have been used in elastomers, adhesives, paints, varnish, printing inks, putty, lubricants, hydraulic fluids, liquid seals, cutting oils, and diffusion pump oils [22]. However, the most recognized use for PCBs was as a cooling fluid and insulator in electrical transformers and capacitors [22, 23, 24].

PCBs are identified in environmental samples throughout the industrialized world, and PCBs have also been detected in pristine regions [22]. PCBs have been identified in many types of wildlife, including fish and waterfowl [22]. PCBs, due to properties which include extreme stability and low polarity, bioconcentrate in species high in the food chain producing enhanced exposures [22]. Exacerbating this problem, PCBs can produce toxicity symptoms in exposed animals, including humans [22]. Human toxicity can include dermatitis, liver damage and jaundice [22].

PCBs were widely recognized as persistent and ubiquitous environmental contaminants by 1973. The FDA established acceptable

ranges of contamination for PCBs in food in 1973, but reduced these levels in 1979 [25]. As an urgent action the EPA banned the manufacture, processing, distribution and use of PCBs in the U.S. in a non-totally enclosed manner in 1977 [26]. Additionally, in 1979 the EPA issued rules for the continued use of devices containing PCBs [25]. Government agencies have placed acceptable upper limits on PCB concentrations in marine water (0.03 ppb), edible fish and shellfish (95 ppm wet weight), workplace air (1 mg/m^3 for Aroclor 1254) and wastewater discharges [27]. However, acceptable levels have been established for PCBs neither in drinking water nor in ambient air [27].

Measurements of PCBs below concentration limits established by regulatory agencies provide several challenges for analytical chemists. PCBs generally exhibit excellent stability, low volatility, and low LODs for GC analyses. However, the 209 possible PCB congeners cannot be completely resolved, even with the best capillary GC columns. Moreover, individual isomers are difficult to obtain in high purity or even at known concentration in reference materials [28]. Thus, the absence of reliable reference materials make determinations of individual PCB isomers difficult, and sometimes not feasible via established ES, IS and SA quantitative methods. Unfortunately regulation has encouraged PCB measurements in units of mass-of-a-specified-Aroclor mixture.

Aroclor mixtures are routinely employed as PCB test materials, even though the concentrations for individual PCB isomers are not well established or are unknown. Aroclor mixtures are obtained by chlorinating biphenyl to achieve a particular specified total

weight percent chlorine [30, 33]. For example, Aroclor 1242 contains 42% chlorine by weight, an average of 3.1 chlorine atoms per biphenyl molecule. However, a single Aroclor mixture contains many different PCB isomers. Researchers have identified many PCB isomers contained in these Arochlor mixtures and measured their relative retention times [29, 30, 31, 32]. PCB isomer identifications and measurements rely heavily on GC-MS analyses [29, 30] and frequently employ NMR techniques [28, 30]. However ambiguities persist for PCB isomer identifications in Aroclor mixtures.

Pattern recognition techniques have been used to compare eluted PCBs with Aroclor mixtures [33, 34, 35, 36]. These techniques employ the Aroclor mixtures as reference materials. Pattern recognition is often used with packed GC columns which do not provide complete resolution of Aroclor components. Chromatograms developed via electron capture detectors (ECD) [34], flame ionization detectors (FID) [35], and mass spectrometry (MS) [36] have been used with pattern recognition for matching Aroclors and PCB samples [33]. PCB determinations in mass of a specified Aroclor generally employ measurements of specific chromatographic peak areas, after an Aroclor match has been asserted [28]. Calculations then estimate how much of that particular Aroclor is in the sample. However, if a gas chromatogram cannot be matched to an Aroclor mixture, then quantitation in units of mass-of-a-specified-Aroclor is not possible [28].

Determination of individual PCB isomers is a proper alternative to pattern recognition techniques. However, to employ established IS, ES and SA methods, an analyte standard must be obtained for

each measured PCB isomer, prior to determination. Consistent with this need, Mullin, et. al. synthesized and prepared an analyte standard for all 209 PCB isomers [28], and characterized chromatographic properties for these analytes. The best capillary GC separations could resolve 187 PCB isomers, but 11 PCB pairs were not resolved.

The ECD provides the lowest LODs for PCBs which contain more than two chlorines, compared to other detectors. However, response factors for ECD measurements of PCBs vary greatly, depending on the particular PCB isomer [37]. Simple shifts in chlorine locations can yield large changes in response factors. Thus, for ECD determinations, available analyte standards and complete chromatographic resolution are required for accurate measurement of individual PCB isomers. Godefoote, et. al. and Millar, et. al. presented methods for PCB determinations in wastewater using the ECD [38, 39].

GC-MS techniques are often used for PCB measurements [40-45]. The LODs for PCBs by GC-MS are usually inferior to LODs for the ECD, but GC-MS offers prospects for PCB identifications. Again, however, PCB determinations by GC-MS require analyte standards for each PCB isomer. PCBs have been measured by GC-MS in fish [30] and water [41].

Webb has characterized Aroclor mixtures with a Coulson detector but did not employ reference materials for each individual analyte [19]. The Coulson detector response was assumed to be linear with organochlorine concentration.

In Section VIII of this thesis, PCB isomer determinations are accomplished in the absence of reference materials for each isomer,

using RFC with GC-HECD. Furthermore, identification of individual PCB eluates is not required. Experiments presented in Section VIII utilize an HECD which has been adapted for use with capillary GC columns.

Electrochemical Detection for GC

The following review of GC detectors summarizes measurement systems which have been published in the scientific literature and utilize electrochemical measurements for the selective detection of GC eluates. The review is mainly intended to provide background on developments related to the Hall Electrolytic Conductivity Detector used extensively in this thesis research.

Development of Electrochemical Detectors for GC

Detectors for gas chromatography have attracted much attention in the field Analytical Chemistry. Detector advancements include improving sensitivity, response time, linear dynamic range, reliability, limit of detection (LOD), and detector selectivity. A highly selective detector can allow for analyte determination from a complex matrix following less sample cleanup than is required when less selective transducers are employed. This is advantageous because sample cleanup may introduce large errors or uncertainties into analyses and cleanup can be laborious. Selective GC detectors [46-50] include electron capture [47, 48, 50-61], alkali flame ionization [47, 48, 50, 62], flame photometric [48, 52, 62, 63],

chemiluminescence [64-66], absorbance and fluorescence [67-70], plasma emission [50, 71, 72-74], mass spectrometry [75-78], and electrochemical detectors [50, 53, 79-85].

Electrochemical detectors for gas chromatography have been recognized as selective detectors which may have a large linear dynamic range. However, limitations in sensitivity, LOD, and reliability have made these detectors unpopular. Most electrochemical detectors for gas chromatography have utilized post-column, high temperature combustion or reduction to yield small inorganic products, or simple measurable species, from column eluents. These simple species are subsequently monitored by coulometry [81, 83-87], potentiometry [80, 88-91] or conductometry [84, 85, 92-109]. Reaction chemistry, gas-liquid interfaces, gas-liquid mixing, and electrochemical detection make detector operation complicated.

Coulometric detectors for gas chromatography have been commercially available. Liberti coupled gas chromatography to a titration cell in 1957 and utilized coulometry to evaluate organic acids [83]. Liberti also used high temperature combustion of column effluents to CO_2 prior to titration. Coulson and Cavanagh coupled gas chromatography in 1960 [82] to a coulometric chloride analyzer [86] utilizing high temperature combustion and determined submicrogram amounts of chlorinated analytes. The Dohrmann Instrument Company commercially marketed an instrument similar to Coulson and Cavanagh's system for the selective detection of halide and sulfur compounds by gas chromatography [87]. In 1966 Martin adapted the Dohrmann Instrument Co. Model C-200 GC detector for the

selective detection of nitrogen compounds by introducing a catalytic reduction of nitrogen to NH_3 prior to coulometric titration [81]. Nitrogen containing analytes were determined below the 10 μg level. The Dohrmann Instrument Company obtained a licensing agreement to commercially market Martin's nitrogen selective coulometric detector. Xertex, Inc., purchased the Dohrmann Instrument Company but presently does not market a coulometric detector for gas chromatography.

Kojina, Ichise and Seo introduced a potentiometric detector for gas chromatography in 1971 [88]. The detector uses post-column high temperature reduction of column effluents with hydrogen over a platinum catalyst. The reduction products are subsequently dissolved in electrolyte solution and measured by ion-selective electrodes. These researchers have utilized the potentiometric detector for selective detection of compounds containing bromine, fluorine, sulfur, nitrogen [80, 89-91], and chlorine containing eluates were detected below the 10 ng level.

Development of Electrolytic Conductivity Detectors for GC

Electrolytic conductivity detectors (ElCD) are the most widely used electrochemical detectors for gas chromatography. Currently, two systems are commercially available from different manufacturers for use in both packed column and capillary gas chromatography. ElCDs provide excellent selectivity for halides, nitrogen or sulfur *vs.* carbon, and may be implemented to have detector response times compatible with capillary columns.

Researchers have criticized ElCD's, claiming poor sensitivities and LODs. However, ElCD sensitivites and LODs are good, although not as good as electron capture detectors (ECD) for most chlorinated hydrocarbons with more than two chlorines per molecule or for halogenated aromatics. However, ElCD detection is usually more sensitive than ECD detection for compounds which contain only one or two chlorine atoms. Also, non-linearities of electron capture and flame photometric systems may compare poorly with the wide linear dynamic ranges of ElCDs. On the other hand, ElCDs typically require more maintenance than many other GC detectors.

Electrolytic conductivity detectors for gas chromatography were developed after the advent of coulometric detectors for GC. Piringer and Pascalau built an ElCD in 1962 which oxidized organic eluents to CO_2 over CuO, mixed gaseous reaction products with electrolyte, and measured a differential conductance signal in the flowing electrolyte [92]. Coulson presented a similar ElCD in 1965, marketed by the Coulson Instruments Company [84]. The combustion system introduced oxygen and column effluent into a high temperature quartz furnace. The products of combustion gas were mixed with aqueous electrolyte and a conductance signal was obtained for the electrolyte after removal of the gas phase. The Coulson detector reportedly could measure 50 ng of Lindane. Tracor Instruments, Inc., purchased production rights for the Coulson detector and marketed the instrument until the Hall Electrolytic Conductivity Detector (HECD) was developed.

Patchett modified the Coulson detector in 1970 to use hydrogen reaction gas in a nickel catalyzed high temperature reduction

furnace [93]. Basic scrubbers were utilized for selective nitrogen detection to remove acid halides from the combustion effluent while passing NH_3. Jones and Nickless further modified the combustion furnace in 1972, miniaturizing the system, reducing heated transfer line lengths, and improving the LOD for chlorinated hydrocarbons to subnanogram levels [94]. Lawrence [95] Cochrane and Wilson [96], and Dolan and Hall [97] evaluated the response of this modified Coulson detector to variations in flow rates and furnace temperatures. Other modifications were made to the Coulson detector by miniaturizing the conductance cell and establishing better electrolyte flow control and temperature control [98-100].

The Coulson detector could be used for the selective detection of GC eluents containing chlorine, nitrogen or sulfur. Selective detection of eluates containing chlorine was a major application for the Coulson detector [84, 94, 96, 97]. However, the electron capture detector was usually preferred over the Coulson detector for selective detection of eluates containing chlorine, due to superior LODs and sensitivities for the ECD. Furthermore, the Coulson detector was cumbersome and required more maintenance than an ECD. Selective detection of eluents containing nitrogen attracted much attention to the Coulson detector since alternative nitrogen selective detectors were not as selective or sensitive for nitrogen [84, 93-95, 98, 99, 101-105]. Sulfur containing eluates were also selectively measured by the Coulson detector [84, 94, 96].

The ElCD was greatly improved by Hall in 1974 [85]. Hall replaced the large, cumbersome, glass Coulson conductivity cell

with a miniturized Teflon and stainless steel cell. The new system combined the gas-liquid contactor, the gas-liquid separator, and a concentric AC conductivity cell into a small, 1 in OD x 2.5 in length, cylindrical unit. The conductivity electrolyte, water in the Coulson detector, was changed to absolute ethanol in the new system to reduce background conductance. A high temperature quartz reactor furnace was used with either H_2 or O_2 reaction gas and heated transfer tubing lengths were reduced. The new system could measure less than 100 pg of Heptachlor.

Tracor Instruments, Inc., ceased to produce the older Coulson detector and purchased rights to manufacture and market Hall's detector. Tracor commercially marketed the new system in 1974 as the Hall Electrolytic Conductivity Detector (HECD) Model 310. MacDonald and King added a venting system to the HECD in 1976 to reduce solvent peak effects [106]. Column effluent was vented to waste prior to the high temperature reactor for 1-2 minutes during solvent peak elution. The venting procedure reduced detector tailing and carbonaceous reactor tube deposits. The venting system and other improvements resulted in the Tracor Model 700 HECD which used 50/50 isopropanol/water as the conductivity solvent instead of absolute ethanol.

Tracor has continued to improve the HECD system. The conductivity cell block was redesigned to include a differential conductivity measurement. A second concentric AC conductivity cell was built into the detector block to measure the electrolyte conductivity prior to the gas-liquid contractor. This reference conductivity measurement of the electrolyte is subtracted from the

conductivity measurement of electrolyte containing dissolved reactor gases to yield a differential conductivity signal. Also, the electrolyte for the halide mode was changed to n-propanol to enhance detector selectivity and reduce noise [107, 108]. The high temperature reactor was again miniaturized, heated transfer lines were eliminated, nickel catalyst tubing replaced quartz reaction tubes, and the entire system was installed in a typical GC detector region. These improvements were combined together in 1978 into Tracor's current Model 700A HECD system. The Model 700A HECD is capable of chlorinated hydrocarbon measurements below the 5 pg level as discussed below. The Tracor Model 700A HECD has improved response time, sensitivity, LOD, physical size and reliability as compared to earlier ElCD's.

Recently, Piringer, who developed the first ElCD for GC in 1962, and Wolff designed an ElCD system for capillary GC columns [109]. The system utilized hydrogen carrier gas, vinyl chloride doped helium auxiliary gas, a high temperature nickel catalyst reactor, and a conductivity cell which does not require a gas-liquid separator. The detector response time is 13 msec and 7.5 pg of Lindane was measured with a S/N ratio of 5. The O-I Corporation introduced a ElCD for capillary GC columns at the 1985 Pittsburgh Conference which appears to be very similar to Piringer and Wolff's system.

The Tracor Model 700A Hall Electrolytic Conductivity Detector for GC

The HECD currently produced and marketed by Tracor Instruments is the Model 700A. The Model 700A is described since the detector was used in many experiments presented in this thesis research. Alterations made to the 700A HECD during experiments are presented in Appendix B, and Appendix C contains noise evaluations of the 700A system.

The Model 700A HECD consists of four physical components: the high temperature reactor, differential conductance cell, electronics module, and the electrolyte pump and resin module (figure 1).

The high temperature reactor combines the catalytic reaction tube, high temperature heater, reaction gas inlet, solvent venting system, and the GC column-HECD interface (figure 2). The high temperature heater consists of a platinum heating element surrounding a 1/4 in OD quartz tube and thermal insulation. Temperature control, based on the linear relationship between the resistance of platinum and its temperature, is achieved by monitoring the potential drop across the platinum heating element and controlling AC power applied to the platinum heating element [110]. The catalytic reaction tube is 1/16 in OD nickel tubing inserted through the quartz tube of the heater. The high temperature region of the nickel tube is approximately 1.5 in. in length.

Reaction gas is introduced into the reactor assembly through a 90° angle inlet located just below the base of the nickel tubing. Gases such as hydrogen, oxygen, or air can be introduced into the

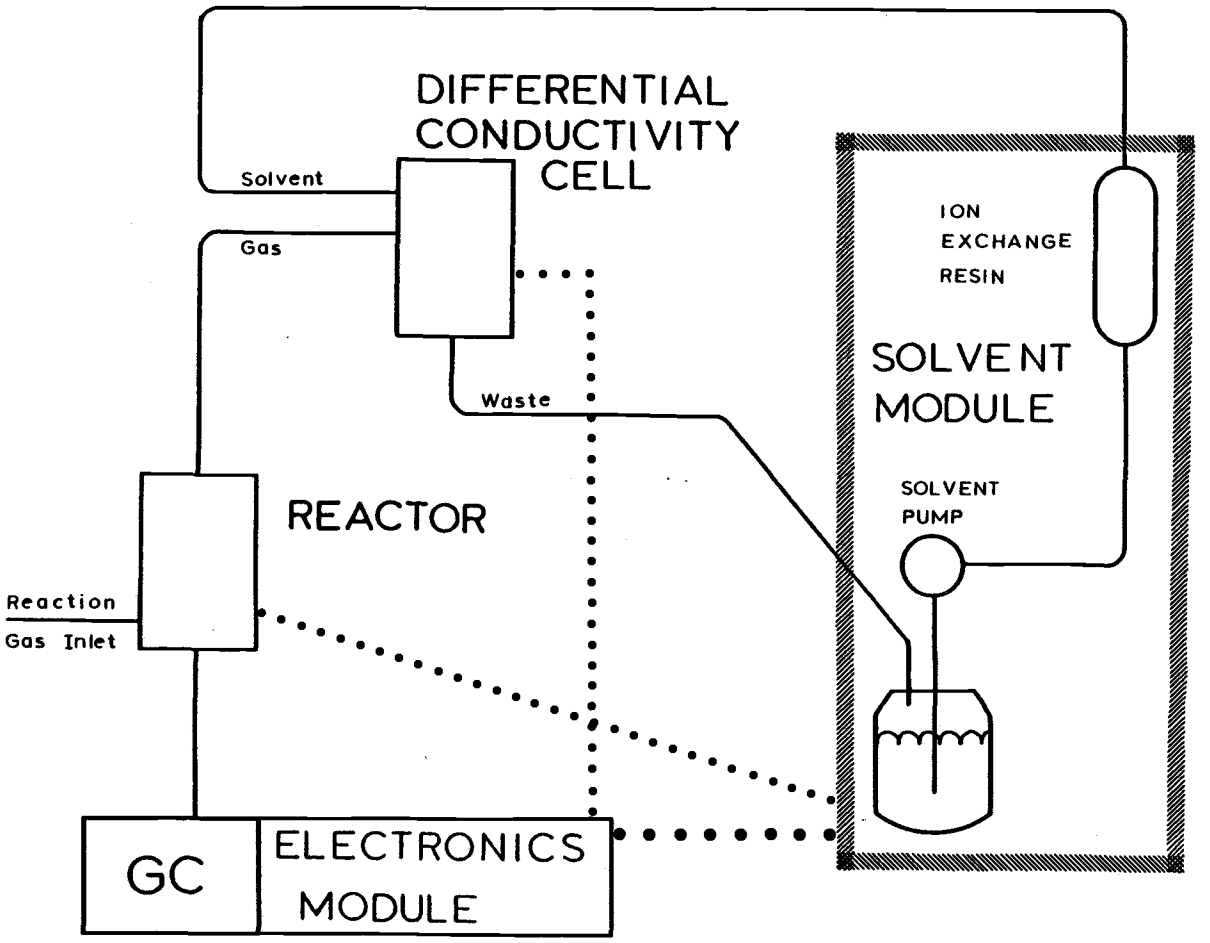

Figure 1. Components of the Tracor Instruments Model 700A Hall Electrolytic Conductivity Detector (HECD).

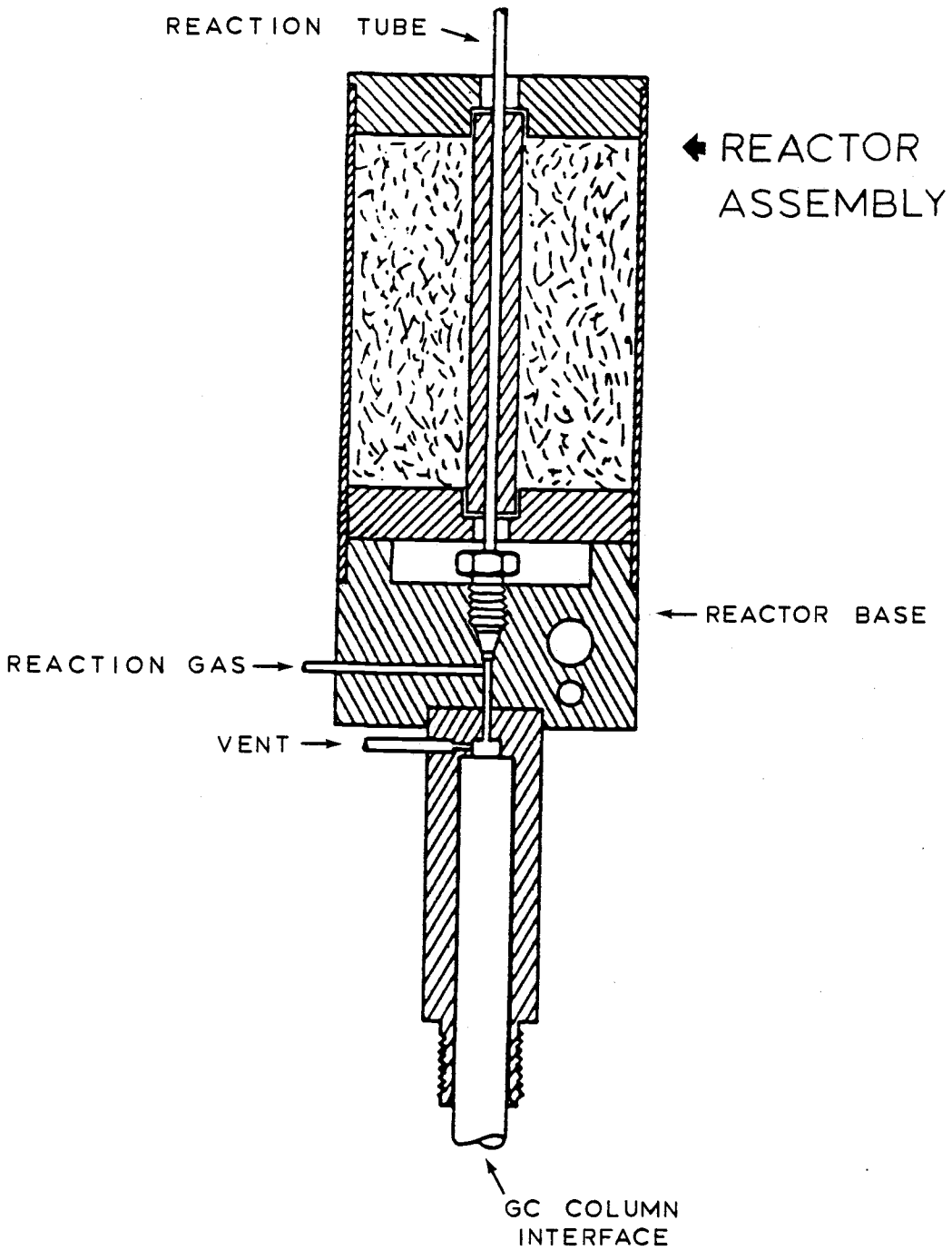

Figure 2. HECD high temperature reactor assembly.

system through this inlet to establish required flow rates and to promote either an oxidizing or reducing environment.

The GC column interface, designed for a 1/4 in OD packed column, is located in the reactor assembly which is heated by a separate temperature controller. A 90° angle outlet, relative to carrier gas flow, is located at the base of the reactor assembly, adjacent to the GC column exit, which leads to a venting solenoid valve. The solenoid is activated manually via the HECD electronics panel to an open position during elution of the solvent peak. The open position normally allows approximately 95 percent of GC column effluent and reaction gas to flow unrestricted to waste while maintaining positive flow through the HECD with the remaining 5 percent flow. The solenoid is deactivated by a preset timing circuit after a selected duration, returning flows to normal operating conditions for the remainder of the elution.

The nickel tube extends approximately one inch above the reactor assembly and effluents are delivered to the differential conductance cell via a 3 in length of 1/16 in OD Teflon transfer tubing or scrubbing devices. Scrubbers selectively remove specified components from the reactor effluent gas which could interfere with conductance measurements, but allow analytes of interest to pass. For example, KOH coated quartz thread, packed into a scrubbing tube, selectively removes HCl or H_2S from the gas stream, yet allows NH_3 to reach the differential conductance cell [111]. Likewise, fine silver wires in a scrubbing tube selectively remove halides from the gas stream, but allow SO_2 and SO_3 to pass [111].

The HECD differential conductance cell is a sophisticated device constructed from stainless steel and Teflon which includes two concentric electrode conductance cells, a gas-liquid contactor, and a gas-liquid separator (figure 3). Conductance solvent is introduced into the reference conductance cell in the upper portion of the cell block. The solvent flows between two concentric electrodes which produce a reference conductance signal. Reactor effluents from the transfer tube or scrubber are mixed with the solvent in the narrow gas-liquid contactor below the reference cell. The stainless steel block is constructed such that the narrow gas-liquid contactor passage exits into a larger volume gas-liquid separator region prior to the analytical conductance cell. The solvent, n-propanol, containing dissolved reactor products adheres to the stainless steel walls of the gas-liquid separator, forming a sheath around the remaining gases which pass through the center. The separated solvent continues to descend along the cell block walls and between another pair of concentric electrodes which produce an analytical conductance signal. The gases exit the cell block through the hollow inner concentric electrode of the analytical cell and solvent passes between the electrodes, exiting through a small hole in the inner electrode.

The reference conductance electrode and analytical conductance electrode responses are monitored by a differential amplifier which produces a differential conductance signal. The excitation signal applied to both conductance cells is a 2.5 kHz, 0.42 V peak to peak bipolar pulse waveform in which every tenth pulse pair is 14 V peak-to-peak (figure 4) [110]. Resulting conductance signals from

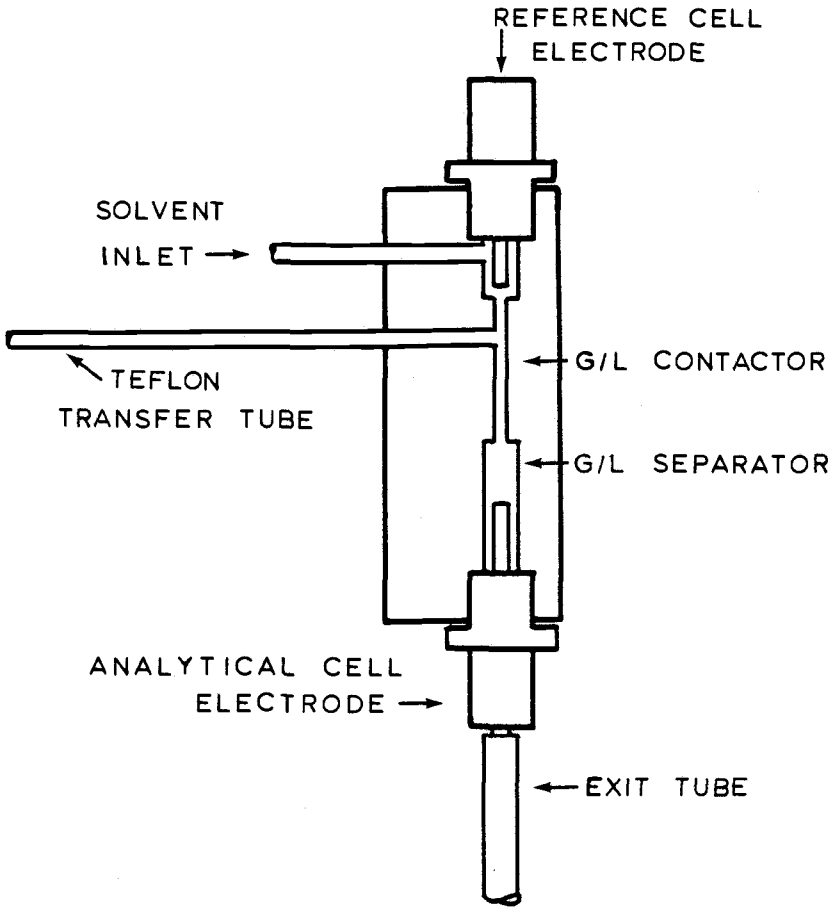

Figure 3. HECD differential conductance cell.

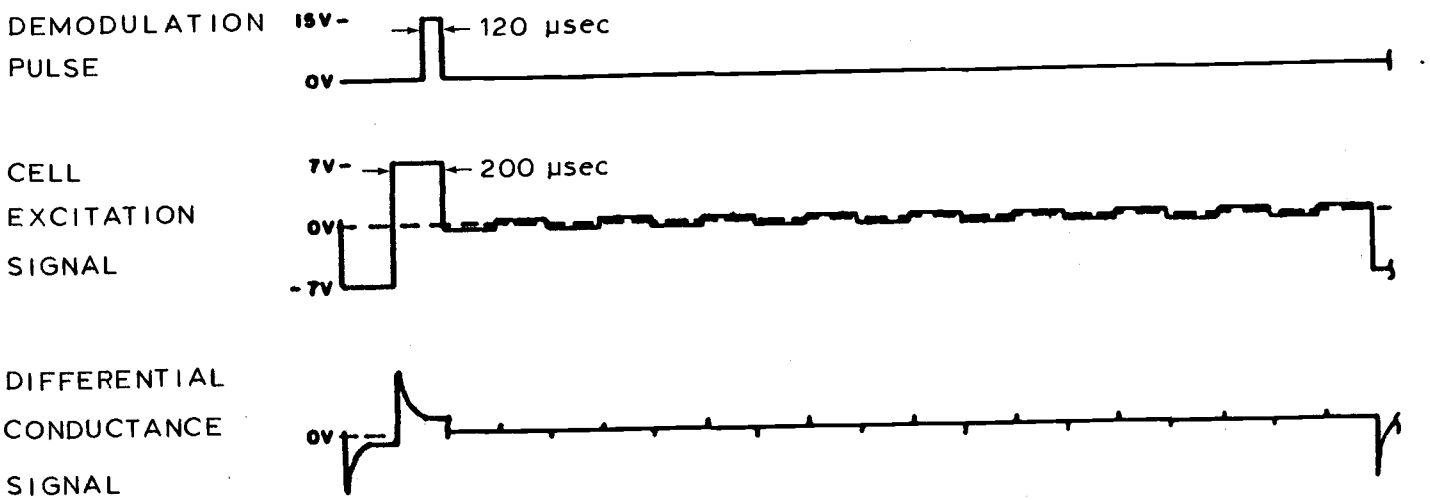

Figure 4. HECD demodulation pulse, cell excitation signal and differential conductance signal.

the reference and analytical cells are selectively demodulated for the final 60 percent of every high magnitude positive pulse to reduce capacitance errors [112, 113]. The high frequency, 2.5 kHz, bipolar signal minimizes electrode polarization. In addition, the low amplitude pulses for 90 percent of the excitation waveform help minimize cell heating, yet allow conductance measurements to be made every 4 msec [112].

Solvent which flows through the differential conductance cell is pumped from a solution reservoir at a constant flow rate, conditioned with an ion-exchange resin bed, delivered to the cell, and recirculated into the solution reservoir. A single piston solvent pump delivers flow rates selected between 0.1 mL/min to 4 mL/min. Pumping pulsations are reduced by the ion-exchange bed. The recommended conductance solvents are n-propanol in the halogen mode, methanol in the sulfur mode, and 50/50 n-propanol/H_2O in the nitrogen mode [110]. Conductance solvents are chosen to enhance analyte solubility, minimize the solubility of potential interferents, and minimize the background conductance signal. For example, n-propanol is used for the halogen mode because H_2S is only slightly soluble compared to HCl, and the background conductance of n-propanol is low [111]. The ion-exchange resins remove potentially interfering ions from the recirculating solutions, and maintain desired pH levels. Acidic resin which contains sulfonate groups, basic resin which contains hydroxylated quarternary amine groups, and neutral resins which contain sulfonate-amine groups are appropriately mixed to produce the desired solvent characteristics.

The pH should be slightly acidic for the halogen or sulfur modes, and slightly basic for the nitrogen mode [111].

Operational Modes for the Hall Electrolytic Conductivity Detector

The HECD, Model 700A, includes five operational modes which target the selective detection of different reactor products. The carbon and nitrosamine modes are used less commonly while the halogen, nitrogen and sulfur modes are often used with the HECD. The different modes require specified reaction tubes, reaction gases, conductance solvents, and scrubbing devices [110].

The halide mode is configured for the selective detection of acid halides, mainly HCl and HBr, arising from catalytic reduction of halocarbon-containing GC eluates. The nickel catalyst reaction tube and hydrogen reaction gas produce a reducing environment within the high temperature reactor, and n-propanol solvent dissolves HCl and HBr but minimizes the solubility of H_2S.

The ion-exchange resin bed usually contains a 50/50 mixture of acid resin ($-SO_3^-H^+$ groups) and neutral resin ($-SO_3^-H^+$ and $-N(CH_3)_3^+OH^-$ groups), and maintains a slightly acidic pH. HCl or HBr contained in the recirculating n-propanol is removed by the ion-exchange resin, producing H_2O which dissolves in the n-propanol solution,

$$H^+ + Cl^- + R\text{-}N(CH_3)_3^+OH \rightleftharpoons R\text{-}N(CH_3)_3^+Cl^- + H_2O \qquad (13)$$

H_2O in reactor gases arising from oxygen-containing GC eluates also dissolves in the n-propanol solution. Likewise, NH_3 in

reactor gases from nitrogen containing GC eluates may dissolve in the acidic electrolyte to produce NH_4^+.

Thus, the observed differential conductance signal will increase in the presence of acid halides from the reactor gases due to the high mobility of H^+ ion in acidic n-propanol. However, the differential conductance signal change due to the presence of H_2S, NH_3 or H_2O in reactor gases is minimized. Consequently, the Model 700A HECD responds with excellent selectively to GC eluents containing halide groups when configured in the halide mode.

Operation in the nitrogen mode is designed to detect NH_3 selectively in reactor gases arising from nitrogen-containing GC eluates. The HECD is used in a manner similar to the halogen operating mode, except that a scrubber containing KOH-coated quartz fibers is used, the ion-exchange resin is mixed to produce a less acidic pH, and the electrolyte is 50/50 n-propanol/H_2O. The scrubbing device removes acids such as HCl, HBr and H_2S from reactor gases while allowing bases such as NH_3 to pass [110]. The detector system responds selectively to nitrogen containing compounds since other reactor products are removed from the reaction gases by the scrubbing device.

Sulfur mode operation provides selective detection of GC eluates containing sulfur groups. The high temperature reactor, equipped with nickel catalyst tubing and oxygen-containing reaction gas, provides an oxidizing environment. A scrubbing device containing fine silver wire removes halides from reaction gases [111].

Methanol treated with a slightly acidic ion-exchange resin is used as the conductance solvent.

Applications for the Hall Electrolytic Conductivity Detector

The Tracor Hall Electrolytic Conductivity Detector, Model 700A, has become an important selective GC detector. Many laboratories have at least one 700A system and regulatory agencies recommend the HECD in many of their approved methods [107, 114]. Review articles which discuss selective GC detectors usually include a detailed presentation of EICDs [48, 49, 63, 115-120].

The Model 700A HECD is used in the halide mode for selective detection of GC eluents containing chlorine. Chlorinated hydrocarbon analyses have been reported with the HECD, following headspace analysis [121, 122] and liquid extraction [123-128]. Because of the excellent selectivity of the HECD, sample preparation procedures even from complex matrices are usually performed easily and do not require derivitization, yet the resulting chromatograms show few interferences. Chlorinated hydrocarbons have been measured in mammalian tissue [124, 125], plant material [127], coal fly ash [128], polymer matrices [122], food materials [123], water samples [121, 126] and air samples [129]. Organochlorine-selective HECD measurements are used to determine trace chlorinated pesticides [124, 125, 127] and water pollutants [121, 126]. Additional selectivity may be achieved via judicious selection of measurement conditions. For example, chlorinated aliphatic hydrocarbons can be measured in the presence of

polychlorinated biphenyls (PCBs) by reducing the HECD reactor temperature until PCBs are not significantly reduced in the reactor [124].

The HECD has excellent LODs and a large linear dynamic range for organochlorine measurements. However, despite these advantages, analysts often reject the HECD in favor of the ECD.

The Model 700A HECD has been used as a selective detector for GC eluents containing nitrogen. Nitrogen-containing mustards [130], benzodiazepin-2-ones [131], barbiturates [132], narcotic alkaloid drugs [133] and nitrogen containing pesticides [134, 135] have been measured from mammalian urine and plasma samples using the nitrogen selective HECD. Other applications of the nitrogen selective HECD include analyses for nitrogen containing compounds in petroleum products [136], coal-liquid fractions [137], polymer matrices [138] and sludges [139]. The alkali flame ionization detector is one of the few alternatives to the HECD for selective nitrogen detection with GC.

Sulfur-containing compounds in hydrocarbon matrices [140, 141], sulfur-containing pesticides in water and soil samples [142] and sulfur-containing hamster pheromones [143, 144] have been measured with the Model 700A HECD operating in the sulfur mode. Operating parameters for the oxidative sulfur mode have been investigated by Ehrlich, Hall, Anderson and Cox [141], and by Gluck [145]. The non-linear flame photometric detector may be used instead of the HECD for the detection of sulfur containing GC effluents.

Applications of the Model 700A HECD reveal this system to be an important detector for GC. Sample matrices analyzed include

biological tissues, biological fluids, food materials, soils, water, air, polymers, and petroleum products. Often less sample preparation is required prior to GC analysis for the HECD than is needed for less selective GC detectors. Frequently analytes such as pesticides, drugs and petroleum products may be selectively measured with the HECD after GC separations.

Unfortunately, purported detector unreliability and other operation difficulties continue to limit use of the HECD. Generally, the HECD is used only when the systems' special properties and characteristics are distinctly advantageous.

III. RESPONSE FACTOR CALIBRATION PROCEDURES FOR CHLORINATED HYDROCARBONS USING GC AND THE HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

A. Determinations of Chlorinated Hydrocarbons by Gas Chromatography Using Response Factor Calibration *

by

Terry L. Ramus, Scott J. Hein and Lawrence C. Thomas

* reproduced with permission from the Journal of Chromatography, Vol. 314, pages 243-251, November 1984.

Summary

The response of the Hall Electrolytic Conductivity Detector (HECD) relative to a response standard may be used to determine unidentified chlorinated hydrocarbons. The HECD can be used as an organic chlorine detector since the response ratio is independent of analyte structure for diverse compounds. The response standard measures the HECD response factor to organochlorine for all analytes determined, similar to an internal standard, but requires neither identification nor identical reference substances for each measured analyte. Response factor calibration uses HECD data for chlorinated hydrocarbons, based upon a response standard, for determinations in units of moles of analyte chlorine. Additional information such as supplemental GC-MS data allows analyte determinations in units of mass. As an example, several chlorinated hexachlorocyclopentadiene photolysis products are determined by using response factor calibration with HECD detection.

Introduction

Quantitation procedures in chromatography generally require that pure reference substances be available from which instrumental response factors can be obtained for each analyte to be determined. Typically, determinations begin with analyte identifications which can be time consuming, or require expensive instruments and experienced technicians. Once analytes are

identified, appropriate reference substances must be obtained via purchase, synthesis or purification from natural origin. Such procedures must be carried out before reliable quantitation can be assured, unless the instrumental response factor for each analyte can be obtained otherwise. Alternatively, response factor relationships are sometimes assumed. For example, in determinations by Gas Chromatography Mass Spectrometry (GC-MS) response factors are sometimes obtained empirically for structurally related compounds [146, 14], although the procedures can be invalid [146, 147]. However, response factors have been obtained for GC with a Hall Electrolytic Conductivity Detector (HECD) in the absence of reliable reference subtances as shown herein.

The HECD is used with GC for quantitation due to its linear dynamic range over five orders of magnitude and its sub-picogram limits of detection [85, 113, 148]. Selectivity for chloride by HECD in the halogen mode is greater than 10^6 relative to carbon and hydrogen [85]. Normally, analyses using the HECD employ reference substances identical with each analyte [148]. However, reliable pure standards are often not available for various reasons, e.g., compound instability, expense, tedious syntheses or purification complications. Despite the absence of reliable reference substances, such compounds may require determination because of their environmental persistence, suspected toxicity or involvement in important reactions. Our evaluation of the HECD, operating in the reducing mode for halide detection, suggests that determinations of chlorinated

organics are possible without separate response factor measurements for each analyte.

Operational Theory for the Hall Electrolytic Conductivity Detector. GC effluents are mixed with hydrogen which then pass through the HECD high temperature nickel catalyst reactor. When an organochlorine compound contacts the catalyst, it reacts to form HCl gas which mixes with n-propanol solvent in a differential conductance cell [113]. The conductance of the n-propanol solution containing the reactor effluent minus the conductance of the n-propanol alone is the HECD differential conductance signal, L. Normally a small baseline conductance, L_o, is observed in the absence of analyte.

Z moles of a resolved chlorinated hydrocarbon, RCl_N, pass through the HECD reactor and upon complete reduction ZN moles of HCl will form. As the ZN moles of HCl pass through the HECD differential conductance cell over time Δt, the total differential conductance signal, L_T, is measured. The integrated differential conductance signal, L_{RCl}, due to ZN moles of HCl is

$$L_{RCl} = \int_{t}^{t + \Delta t} (L_T - L_o)\, dt = \frac{(\lambda_{H^+} + \lambda_{Cl^-})}{\ell/A \cdot V_c} \cdot ZN \qquad (14)$$

where λ_{H^+} and λ_{Cl^-} are equivalent ion conductivities, V_c is the cell volume and ℓ/A is the cell constant [149]. These terms are unchanged at constant temperature and low

dilutions [149, 150], such that under typical HECD operation conditions L_{RCl} = constant · ZN.

L_{RCl} is therefore predicted to be proportional to ZN and independent of the specific analyte structure if catalytic degradation of organic chlorine to HCl is analyte independent. In practice, the proportionality may depend upon carrier gas and hydrogen flow rates, furnace temperature and n-propanol flow rates [85]. However, the ratio of L_{RCl} to the integrated conductance signal for a response standard will be constant if the HECD conditions remain unchanged during their elution. This response ratio is related to analyte organic chlorine equivalents. Unlike traditional internal standard methods, it does not require an identical reference compound for the determination of each analyte [151]. Our assertion of analyte independence is consistent with Lopez-Avila who stated that the response of the HECD in the halogen mode was roughly proportional to the number of chlorine atoms present, although deviations were observed for some p-chloroanilines and chloronitroanilines [148]. However, these chloroanilines contain nitrogen.

The results indicate that a single calibration curve may be used for analytes which contain only carbon, hydrogen and chlorine. Response factor calibration (RFC) is demonstrated, using the HECD for analyte determinations without reference substances for each analyte.

Experimental

Reagents. Reference substances to evaluate the HECD response were purchased from Aldrich Chemical: 1-chlorooctane (1COA, 99% pure), 1,2,3-trichloropropane (TCPrA, 99+% pure), 1,5-dichloropentane (DCPeA, 99% pure), 1-chlorobenzene (CB, 99% pure), 1,2,4-trichlorobenzene (TCB, 99+% pure) and hexachlorobutadiene (HCBD, 98% pure). Technical grade pentachloroethane (PCEA) received from the British Drug Houses was purified by vacuum distillation to greater than 99.5% purity. Reference solutions were provided by the U.S. Environmental Protection Agency: β-hexachlorocyclohexane (β-HCCHA, 99+% pure) and Aldrin (97+% pure). Purity for each of the reference substances was confirmed by GC-HECD and GC-FID.

Hexachlorocyclopentadiene (HCCPD), purchased from Aldrich Chemical, was used in photolysis experiments. Resi-analyzed grade n-hexane and n-propanol solvents were purchased from J.T. Baker Chemical Co.

Procedures. 1COA was chosen to be the response standard due to its high purity and stability. Solutions of 1COA were prepared at concentrations of 5.89×10^3 nmol Cl/mL, 589 nmol Cl/mL and 59 nmol Cl/mL.

The eight chlorinated hydrocarbons were divided into four subsets such that all the compounds were resolved by GC-HECD. Group I included 1COA, TCPrA and DCPeA; Group II included 1COA, CB and TCB; Group III included 1COA and HCBD; and Group IV

included 1COA, PCEA, β-HCCHA and Aldrin. β-HCCHA and Aldrin solutions were diluted from 2.5 mg/mL and 5.0 mg/mL standard solutions, respectively.

Solutions of the eight compounds were prepared as groups at eight to ten concentrations each, ranging from about 0.3 nmol Cl/mL to 1.3 X 10^3 nmol Cl/mL. 10 mL of a 1COA response standard was added to each solution prior to complete dilution. Acid washed, hexane rinsed glassware was used in all dilutions and storage. Class A volumetric glassware, Kirk design micropipets and n-hexane were used for all dilutions. Concentrations were calculated using known densities, molecular weights and molecular formulas [152].

A 1.7 mg/mL HCCPD solution was prepared in n-hexane. Subsamples of this solution were photolyzed under a Sylvania F15T8-BL Ultraviolet Blacklite. Following UV exposure, each subsample was diluted by a factor of 100 and evaluated in triplicate using HCCPD as an external response standard.

Chromatographic Instrumentation. A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was used with a 2m X 2mm ID glass column, packed with 3% OV-17 on 100/120 Supelcoport. Airco grade 4.5 helium was used as the carrier gas at 30 mL/min. Airco grade 4.5 hydrogen with a hydrocarbon trap was used as the HECD reactor gas at 60 mL/min. The HECD conductivity solvent, n-propanol, was pumped at 0.5 mL/min. The nickel catalyst reactor temperature was 850 °C, the HECD base temperature was 300 °C and the GC injector temperature was

250 °C. GC sample injection volumes were 1 μL. A Hewlett-Packard Model 3390A integrator was used to determine the GC peak areas and retention times.

Group I compounds were separated by a GC temperature program from 30 °C to 70 °C, increased at 3 °C/min, after a 5 min. isothermal period at 30 °C. Group II compounds were resolved by a program from 30 °C to 75 °C at 4 °C/min. after a 5 min. isothermal period at 30 °C. Group III compounds were separated using a 3 min. isothermal period at 50 °C followed by temperature programming to 100 °C at 4 °C/min. The compounds in Group IV were resolved using a 5 min. isothermal period at 30 °C followed by temperature programming to 250 °C at 3 °C/min. The HCCPD subsamples were analyzed using a temperature program from 60 °C to 200 °C, at 3 °C/min, after a 5 min. isothermal period at 60 °C.

GC-MS data were obtained on a Hewlett-Packard Model 5890A GC-MS interfaced by a membrane separator. The mass spectrometer used electron impact ionization at 70 eV. The same gas chromatographic parameters were used as descibed above.

Results

The HECD response is predicted to be proportional to the amount of organic chlorine, as discussed above. To test this prediction, responses for a variety of chlorinated hydrocarbons were evaluated with the HECD. Preliminary experiments revealed

that the HECD sensitivity changed slowly with time, but remained constant during individual chromatograms, e.g., 40 min. A response standard, 1-chlorooctane (1COA), was used in these experiments to compensate for intersample changes in the detector response, variations in sample volumes, and to act as the reference substance for analyte determinations. Thus, a response ratio was defined as the analyte peak area, A_u, divided by the peak area for the 1COA, A_{rs}.

Analyte concentrations ranged over four orders of magnitude from 0.3 nmol Cl/mL to 1.3 μmol Cl/mL or from 13 ng of HCBD/mL to 110 μg of CB/mL. Table 1 shows the groupings of the eight compounds evaluated, the number of dilutions per compound, the concentration ranges, and the number of determinations.

Calibration Curve. The data illustrated in figure 5 indicate a linear correspondence between the response ratio and the organic chlorine concentration. Curve fitting was performed by a linear least squares regression technique on the logarithmic data, as recommended when data extends over several orders of magnitude [154]. Log-log regression parameters and log-log parameter 90% confidence limits are given in Table 1 [153, 155]. Of 331 data points, 4 were excluded because their concentrations were below the limit of detection, and 3 were deleted because of a confirmed pipeting error. The regression line calculated from the remaining 324 data points is shown in figure 5. Figure 5 also contains 75 means from replicate injections of 75 different concentrations among the eight compounds tested.

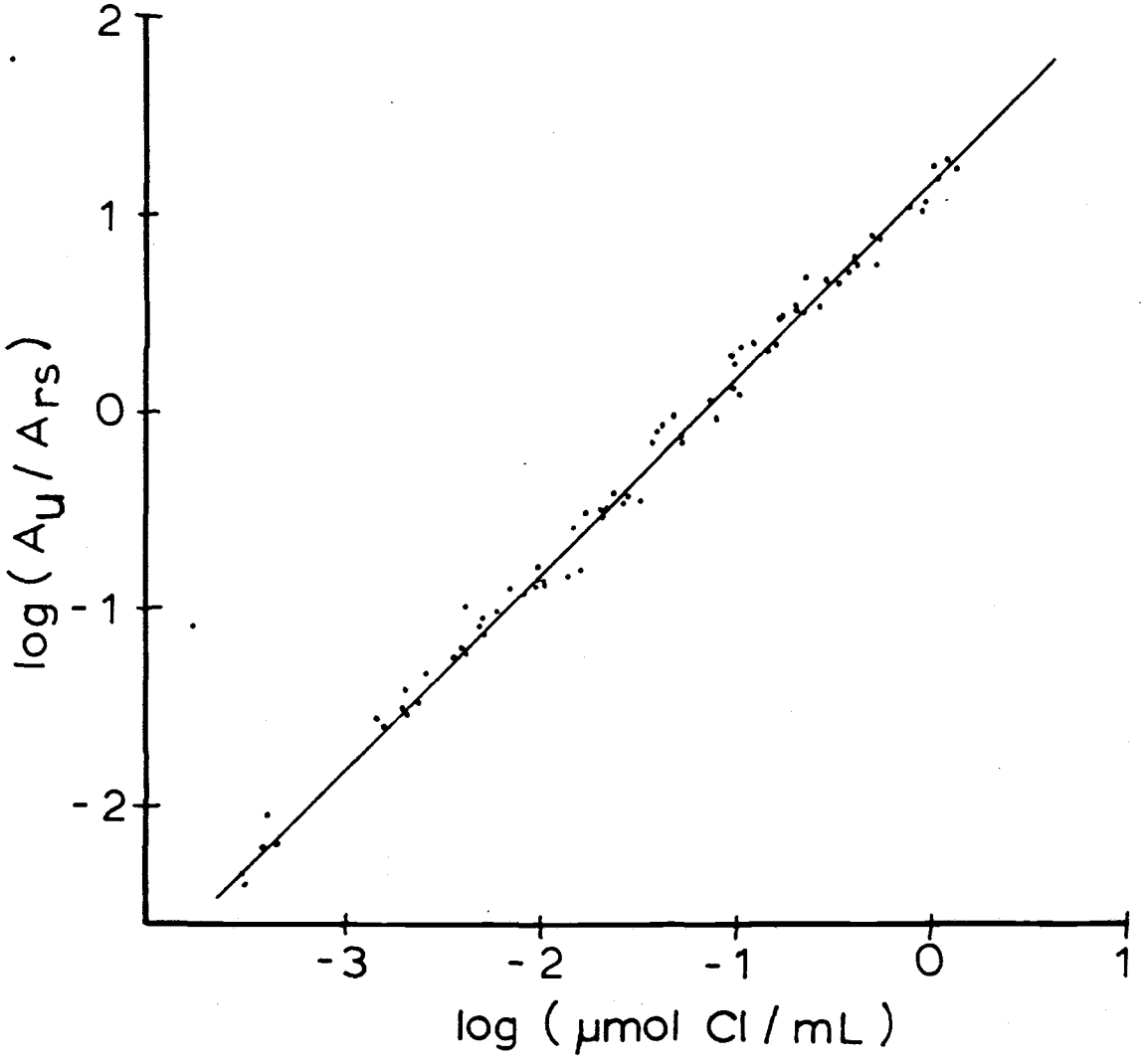

Figure 5. Log-Log plot of the response ratio vs. µmol of analyte organic chlorine. a) points (•) represent means obtained from replicated sample injections. b) log-log regression line (——).

Table 1. Response factor calibration data, log-log regression parameters and parameter 90% confidence limits for eight chlorinated hydrocarbons.

Group	Compound	n[a]	Number of Dilutions	Conc. Range nmol Cl/mL	Log-Log Regression Parameters			
					m_L[b]	90% Conf. Limits-m_L	b_L[c]	90% Conf. Limits-b_L
I	TCPrA	28	10	2.8-710	0.99	0.03	1.16	0.02
I	DCPeA	28	10	3.1-780	0.99	0.03	1.09	0.03
II	CB	45	10	3.9-980	1.01	0.03	1.24	0.01
II	TCB	45	10	0.48-1200	1.05	0.02	1.29	0.01
III	HCBD	83	10	0.28-960	1.01	0.03	1.20	0.01
IV	PCEA	34	9	2.1-1040	1.00	0.05	1.20	0.03
IV	β-HCCHA	33	9	2.6-1290	0.94	0.04	1.06	0.02
IV	Aldrin	28	8	4.1-820	0.90	0.05	1.13	0.05
All Compounds		324	75	0.28-1290	1.00	0.01	1.20	0.003

[a] total number of HECD measurements for the compound. [b] slope of log-log regression line. [c] intercept for log-log regression line.

These data demonstrate the linear relation between the response ratio and organic chlorine concentration since the slope of the log-log plot doesn't differ significantly from unity. Also, the response ratio did not require correction for a nonzero y-intercept prior to logarithmic curve fitting. The eight separate log-log regression lines for each of the eight compounds evaluated are shown in figure 6.

Photolysis Product Determinations. HCCPD photolysis products were determined using HECD detection and response factor calibration (RFC). A 1.7 mg/mL solution of HCCPD in n-hexane was evaluated following exposure to UV light for 26 hours. The chromatogram in figure 7 includes unreacted HCCPD and three unidentified photolysis products. Mass Spectral data was obtained by GC-MS for the unidentified photolysis products. The molecular weight of the first product could not be determined. The second product was present below the limit of detection for our GC-MS. The number of chlorines per molecule and the analyte molecular weight was determined for the third unidentifed product. Analyte concentrations were determined in the diluted aliquots for HCCPD and the unidentified photolysis products by RFC via an external response standard (Table 2).

Discussion

The utility of response factor calibration was demonstrated by using the HECD. Eight chlorinated hydrocarbons with different

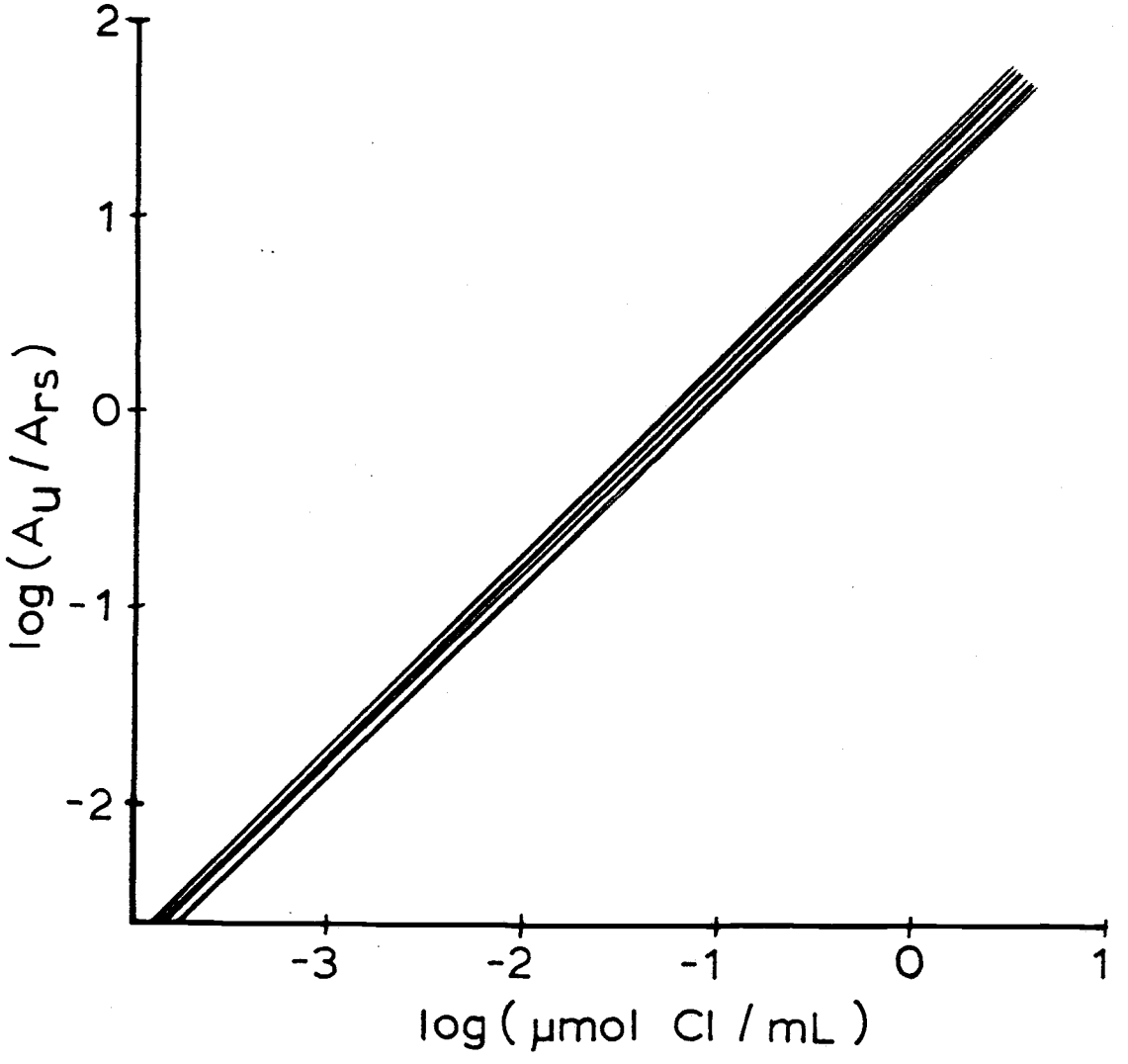

Figure 6. Log-log regression lines for response ratio vs. µmol of analyte organic chlorine. Each line corresponds to all measurements for each of the eight compounds.

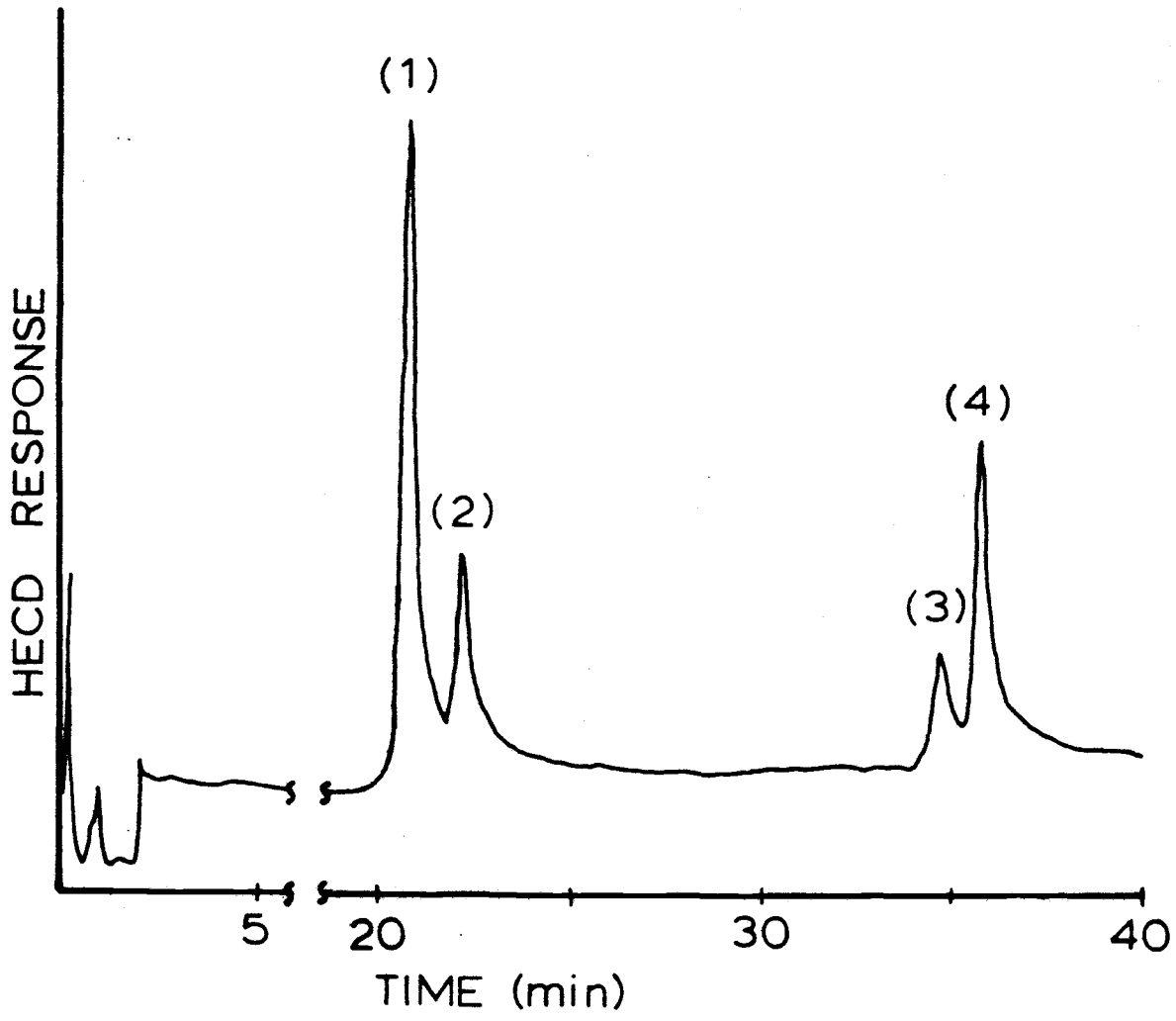

Figure 7. HECD chromatogram of HCCPD photolysis products. (1) HCCPD, (2), (3) and (4) unidentified HCCPD photolysis products.

Table 2. Response factor calibration method data for HCCPD photolysis product determinations in the diluted aliquots, following UV exposure for 26 hrs.

Peak	nmol Cl / mL	Cl / Molecule	nmol Analyte / mL	Molecular Weight	ng Analyte / mL
1	48.	6	7.9	272.8	2200
2[a]	14.	NA[b]	NA[b]	NA[b]	NA[b]
3[a]	10.	NA[c]	NA[c]	NA[c]	NA[c]
4[a]	26.	8	3.2	343.7	1100

NA - not applicable. [a] Analyte identity unknown. [b] Molecular ion mass not established. [c] Analyte below limit of detection.

structural characteristics all result in the same HECD response ratio calibration curve (figure 5). Individual log-log regression lines for each of the eight chlorinated hydrocarbons evaluated reveal small proportional errors since their parallel lines correspond to eight lines of different slopes on a linear plot (figure 6) [156]. Possible sources of proportional errors include: (a) minor impurities in the reference substances, (b) small changes in carrier gas flow rate during temperature programming, and (c) inaccuracies in density values. However, log-log regression slope and intercept parameters for the eight separate regression lines could not be shown to be different by Q-tests or by null hypothesis tests based on the t-statistic at the 90% confidence level [153, 157].

Response Factor Calibration (RFC). These studies suggest that analytes containing only carbon, hydrogen and chlorine may be determined without identical reference substances using response factor calibration. A response standard of known purity and chlorine composition must be available which is resolved from the analytes. It may be added to samples for analysis, like an internal standard, but the response standard also functions as the reference substance for all analytes determined. Alternatively, a response standard may be measured during a different elution, like an external standard, if HECD conditions remain constant.

RFC using only HECD data allows for analyte determinations in moles of organic chlorine, X_u. X_u is calculated from the response ratio, A_u/A_{rs}, the log-log calibration slope which is

unity, m_L, and log-log intercept, b_L, as

$$X_u = (A_u / A_{rs}) \cdot 10^{-b_L} . \qquad (15)$$

If the number of chlorine atoms per molecule, N_u, can be determined via isotope ratios from the analyte mass spectrum [158], then the moles of analyte is $Z_u = X_u/N_{Cl}$. If the molecular ion mass, MW_u, is obtained from GC-MS data, then the analyte mass may be calculated in grams, $M_u = Z_u \cdot MW_u$. When analyte identity is known, N_u and MW_u are known, and mass spectral data is not required for analyte determination in grams.

RFC requires the following for chlorinated hydrocarbon measurements with the HECD: (a) the analytes and response standard are resolved, (b) the analytes do not contain elements which interfere with the HECD signal, (c) complete analyte reaction to HCl in the furnace, (d) the HECD response factor to organochlorine remains constant during a single chromatogram, and (e) differential conductance cell flow rates remain constant during a single chromatogram.

HCCPD Photolysis Product Analysis using RFC. RFC was demonstrated in the HCCPD photolysis product experiments described above (Table 2), assuming interferents were not incorporated during photolysis of HCCPD in hexane. Unreacted HCCPD was determined in nanograms since peak identity was known and thus N_u and MW_u were known. Peak 2, an unidentified photolysis product, was determined in nmol of chlorine since the analyte molecular weight could not be identified. Peak 3, another unidentified photolysis product, was

determined in nanomoles of chlorine since the analyte was present below the GC-MS limit of detection. The last unidentified photolysis product, peak 4, was determined in nanograms from the molecular weight and number of chlorines per molecule obtained by GC-MS [158].

The HCCPD photolysis product measurements were accomplished rapidly, without identical reference substances for the unidentified analytes. The concentrations of HCCPD and photolysis products were also followed as a function of exposure time without time consuming identification and preparation of reference substances.

Reservations About RFC Data. We have evaluated chlorinated hydrocarbons of diverse structure and have encountered no exceptions to the developed HECD calibration curve, although such compounds may exist. If exceptions are found, they might be corrected by adjusting reactor temperature [112]. Chlorinated compounds which include other substituents and HECD furnace temperature effects are presently being evaluated in our laboratory.

Certainly, reservations exist for RFC determinations of unidentified analytes since these compounds may unknowingly include functional groups or elements which might cause deviations from the HECD calibration curve. However, RFC may be used for measuring unidentified analytes in the absence of reference substances in complex samples at low concentrations. Therefore, we recommend judicious use of RFC data for unknown analytes, until analyte

identification or identical reference substances permit more complete study.

Application Of RFC To Other Detection Systems. Other instrumental methods might also be adapted to RFC. To use RFC, the detection system must meet several requirements: (a) a known response versus concentration relationship for the measured chemical species, (b) a detector response factor for the measured chemical species which is independent of analyte origin, and (c) a constant response factor during elution of analytes and the response standard.

B. Other Studies on Determinations of Chlorinated Hydrocarbons by GC Using Response Factor Calibration

Response factor calibration has been demonstrated for the determination of chlorinated hydrocarbons with GC-HECD by experiments presented above in Section IIIa. RFC was presented, evaluated with chlorinated hydrocarbon test materials, and applied to the determination of three HCCPD photolysis products. This section provides additional information from related experiments.

Calibration Curves for Chlorinated Hydrocarbon Determinations with RFC

Calibration curves are often obtained by fitting selected mathematical models to data from analyses of analyte standards via least squares regression techniques. Many calibration curves are appropriately represented by a straight line, $y = mx + b$, when transducer response is linearly related to analyte concentration. Accordingly, the HECD response ratio in RFC was shown in Section IIIa to be linearly related to the analyte organochlorine equivalents over four orders of magnitude for chlorinated hydrocarbons. That is, analyte standards of chlorinated hydrocarbons were evaluated by RFC and modeled by linear least squares regression to obtain a linear calibration curve.

Linear least squares regression techniques assume that variance in the dependent variable, y, is constant along the calibration curve over the range of the data set [161]. However, in this research the variance in chromatographic peak areas, for chlorinated hydrocarbons used to develop the calibration curve for RFC, increases with increased analyte organochlorine equivalents. Residuals for larger-magnitude data corresponding to higher organochlorine equivalents therefore dominate the best fit obtained by linear regression, producing uncharacteristically large imprecision for lower organochlorine equivalents [154]. Weighting the data according to the inverse of the variance at each level may partially compensate for such non-uniform variances. However, weighting requires that estimates of the variances be obtained at each measured level of analyte organochlorine equivalents [154, 159, 160].

Alternatively, data transformation can be used prior to regression techniques to minimize effects of non-uniform variances [161-163]. For example, Kurtz recommends using log-log least squares regression with chromatographic data for developing calibration curves over large dynamic ranges [154]. Log-log regression yields uniform confidence intervals over a broad dynamic range which are proportional to analyte concentration [154]. This direct relationship between confidence intervals and analyte organochlorine equivalents is consistent with trends observed in RFC data for chlorinated hydrocarbons determined by GC-HECD. Furthermore, log-log transformation does not require estimates of variance at each analyte concentration level. Agterdenbos also recommends log-log

regression for developing calibration curves with chromatographic data [160].

The 324 response ratio measurements, obtained for the chlorinated hydrocarbon concentrations listed in Table 1, were related to the analyte organochlorine equivalents by log-log least-squares regression as

$$\log\left(\frac{A_u}{A_{rs}}\right) = m_L \log\left[X_u\right] + b_L \qquad (16)$$

The log-log regression yielded $m_L = 1.00 \pm 0.01$ and $b_L = 1.20 \pm 0.003$, where the uncertainties are the 90% confidence intervals for the regression parameters based upon the student's t-statistic [153]. Equation 16 can be simplified to,

$$\frac{A_u}{A_{rs}} = X_u \cdot 10^{b_L} \qquad (17)$$

since m_L is unity i.e., the response ratio *vs.* chlorine equivalents relation is linear. Thus, analyte organochlorine equivalents may be calculated from the measured response ratio and the intercept of log-log calibration curve.

The same 324 data points were also modeled by a linear least-squares regression,

$$\frac{A_u}{A_{rs}} = m X_u + b \qquad (18)$$

The linear regression yielded $m = 15.1 \pm 0.3$ and $b = 0.07 \pm 0.08$,

where the uncertainties are the 90% confidence intervals for the regression parameters based upon the student's t-statistic [153]. Thus, b is not significantly different from zero at the 90% confidence level. Comparing equation 18 to equations 9 and 11 reveals that 1/m is equivalent to X_{rs} since b is zero. Thus, the $10^{b}L$ term in equation 17 is equivalent to m, and $10^{-b}L$ is equivalent to the X_{rs} term in equations 9 and 11. Experimentally, $10^{-b}L$ is calculated to be equivalent to X_{rs} within 6% for these 324 data points.

Confidence Intervals for RFC Determinations. 90% confidence interval estimates were calculated from the least squares variance at 0.10 μmol Cl/mL, near the middle of the calibration curve (figure 5), using quantities obtained from the log-log regression. 90% confidence interval calculations are based upon the student's t-statistic. The corresponding 90% confidence interval estimate for the point corresponding to 0.10 μmol Cl/mL on the calibration curve is a response ratio of 1.57 ± 0.05, or ± 3% [154]. The 90% confidence interval estimate for organochlorine equivalents at a response ratio mean of 1.57, obtained from ten replicate measurements of a sample, is 0.10 ± 0.015 μmol Cl/mL, or ± 15% [153]. This final 90% confidence interval estimate is dependent on the number of sample measurements used to calculate the response ratio mean.

Effects of Constant Carrier Gas Flow and Reactor Temperature on the RFC Calibration Curve for Chlorinated Hydrocarbons. Response

factor calibration analyses with GC-HECD should employ reactor temperatures in excess of 950 ^{o}C and constant carrier gas flow. Experiments supporting these requirements for RFC are presented in Section IV and V. However, the calibration curve developed for chlorinated hydrocarbon determinations by RFC with packed column GC-HECD employed a reactor temperature of 850 ^{o}C and did not utilize constant carrier gas flow. Thus, chlorinated hydrocarbon standards were reanalyzed after implementing reactor temperatures above 950 ^{o}C and carrier gas flow control.

The 26 data points achieved at 950 ^{o}C with flow control were modeled by log-log regression to yield m_L = 1.05 $\pm$ 0.05 and b_L = 1.20 $\pm$ 0.06. The same data were also modeled by a linear regression to yield m = 15.9 $\pm$ 0.8 and b = -0.07 $\pm$ 0.4; again b was not significantly different from zero and m_L was not significantly different from unity: the stated uncertainties are the 90% confidence intervals for the regression parameters based upon the student's t-statistic [153]. Thus, regression parameters for the log-log calibration curve obtained from these additional experiments were not significantly different from the log-log calibration curve obtained in Section IIIa.

These evaluations indicate that slightly lower reactor temperatures and the absence of carrier gas flow control did not substantially affect measurements for these particular chlorinated hydrocarbons nor alter the calibration curve. This was not unexpected as the absence of constant carrier gas flow should not introduce significant errors for the short temperature programs used in these analyses, i.e. ΔT = 40 ^{o}C. Similarly, a reactor

temperature of 850 °C did not introduce significant errors due to poor analyte reduction efficiencies for these particular chlorinated hydrocarbons. However, other analytes show significant reactor temperature dependencies (see Section IV).

HCCPD Photolysis Product Analyses Using RFC with GC-HECD and a 1-chlorooctane Response Standard

The HCCPD photolysis product experiment presented in Section IIIa was repeated using HECD reactor temperatures of 950 °C, constant carrier gas flow, and a 1COA response standard. A solution of 1.7 mg/mL HCCPD in n-hexane was subdivided into 15 mL aliquots and exposed to UV light for 26 hours. Six aliquots were removed after different exposure times. Exposed aliquots were diluted by a factor of 100 with n-hexane and 1COA response standard was included at 8.75 µg/mL.

Figure 8 contains an HECD chromatogram from a diluted aliquot of HCCPD solution exposed to UV light for 26 hours. Analyte concentrations for HCCPD and the three unidentified photolysis products were determined in the photolysis solution by RFC in µmol Cl/mL and µg/mL as shown in Table 3. The two separate HCCPD photolysis experiments used a UV exposure chamber which did not control temperature nor monitor light intensity. However, these two separate experiments, summarized in Tables 2 and 3, yield HCCPD concentrations which agree within 5% following UV exposure for 26 hours.

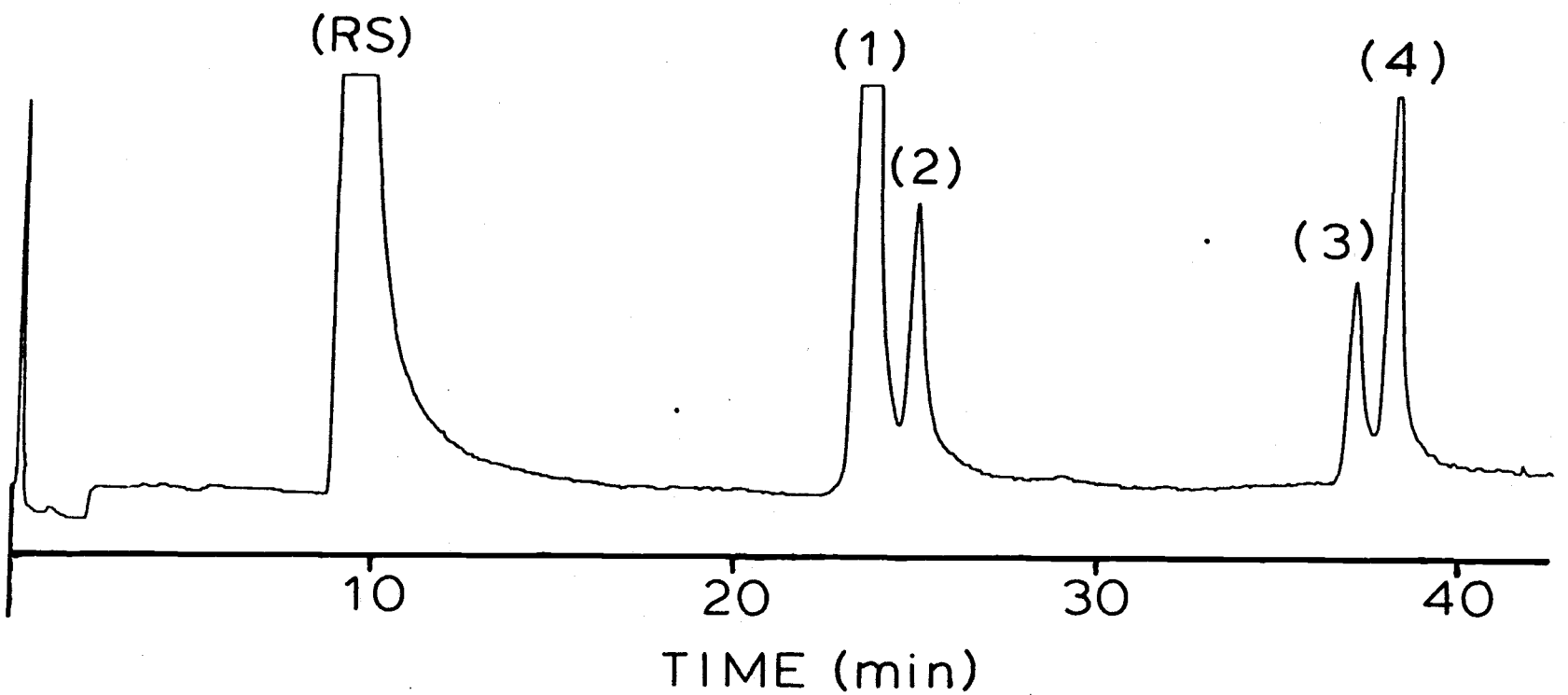

Figure 8. HECD chromatogram of HCCPD photolysis products and 1COA response standard (RS). (1) HCCPD, (2), (3), (4) unidentified HCCPD photolysis products.

Table 3. HCCPD photolysis product determinations in the photolysis solution following UV exposure for 26 hours by RFC with ICOA response standard.

Peak	µmol Cl / mL	Cl / Molecule	Molecular Weight	µg Analyte / mL
1	4.7	6	272.8	210
2[a]	0.6	NA[b]	NA[b]	NA[b]
3[a]	0.4	NA[c]	NA[c]	NA[c]
4[a]	0.8	8	343.7	36

NA - not applicable. [a] Analyte identity unknown. [b] Molecular ion mass not established. [c] Analyte below limit of detection.

As above, photolysis product identities were not established, and neither the number of chlorines per molecule nor molecular weight were obtained for two of the photolysis products. However, using RFC determinations in µmol Cl/mL, the unidentified analytes were quantitatively measured over the duration of the photolysis experiment. Figure 9 contains a graph of the analyte concentrations as UV exposure time increases. The HCCPD concentration, chromatographic peak #1, decreases by 86% from 33 µmol Cl/mL or 1.5 mg HCCPD/mL at exposure time zero to 4.7 µmol Cl/mL or 210 µg HCCPD/mL after an exposure time of 26 hours. The HCCPD solution was nominally prepared at 1.7 mg HCCPD/mL, however, the measured concentration prior to exposure is 1.5 mg HCCPD/mL. Differences between prepared and observed HCCPD concentrations at initial exposure are perhaps due to HCCPD degradation during storage. The changes in photolysis product concentrations are shown in figure 10. Unknown product #2, chromatographic peak #3, was originally present at 0.15 µmol Cl/mL as an impurity, corresponding to 0.4% of the total organochlorine content prior to photolysis. The concentrations of the three unidentified products, following UV exposure for 26 hours, were highest for unknown #3, followed by unknown #1 and unknown #2, respectively (figure 10).

The degradation of HCCPD due to photolysis was followed quantitatively by RFC with GC-HECD, and unidentified photolysis products were measured. The experiment did not require prior identification of these analytes nor the use of reference materials which contain these identical analytes.

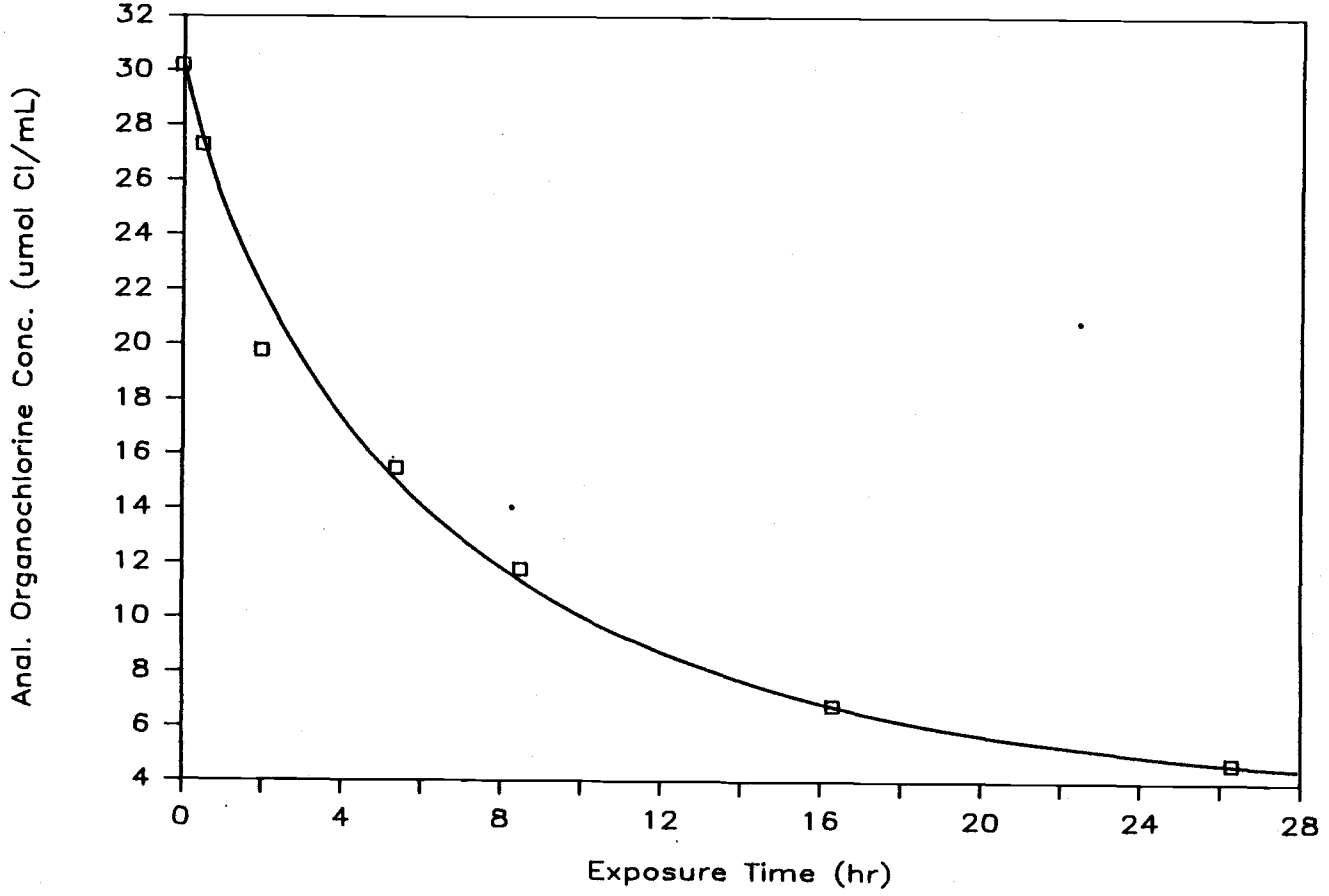

Figure 9. HCCPD photolysis degradation during exposure to UV light. RFC and GC-HECD were used for quantitative measurements.

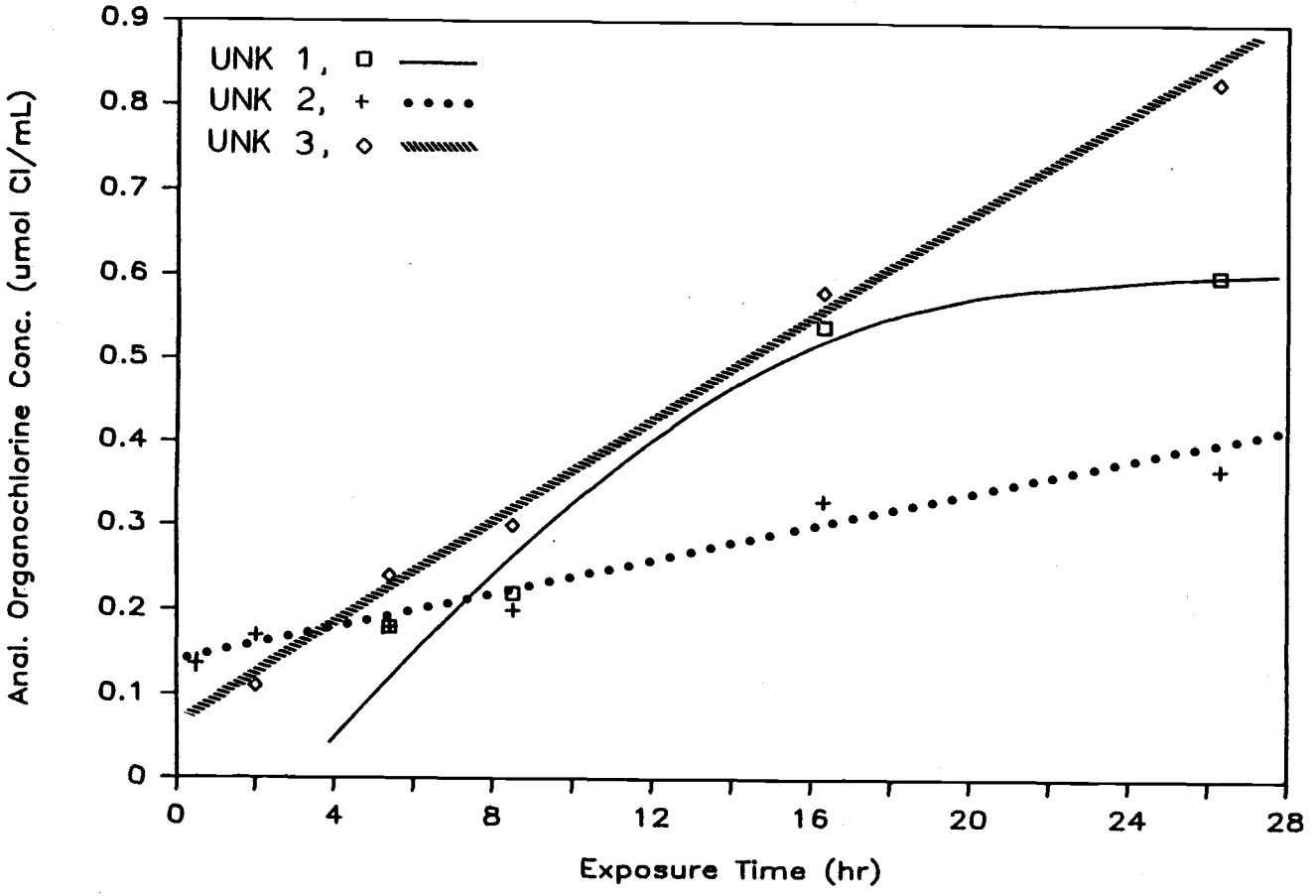

Figure 10. HCCPD photolysis products resulting from HCCPD exposure to UV light. RFC and GC-HECD were used for quantitative measurements.

IV. TEMPERATURE SELECTION FOR CHLORINATED HYDROCARBON REDUCTION FOR THE HALL ELECTROLYTIC CONDUCTIVITY DETECTOR *

by

Terry L. Ramus and Lawrence C. Thomas

* reproduced with permission from the Journal of Chromatography, Vol. 328, pages 342-346, 1985.

Summary

A Hall Electrolytic Conductivity Detector (HECD) reactor temperature of at least 950 °C is recommended for chlorinated hydrocarbon determinations which require a constant HECD response factor, unless another temperature is properly justified. Temperature dependencies of chlorinated hydrocarbon reductions in the HECD are shown. Several test compounds were not completely reduced at reactor temperatures below 950 °C. Additionally, variable reduction yields were observed for the compounds at 800 °C. However, mass spectra of HECD reactor effluents at 950 °C corresponded to quantitative reductions yielding HCl.

Introduction

The Hall Electrolytic Conductivity Detector (HECD) has been used in determinations for which the HECD response factor must be equivalent for several chlorinated compounds [20, 128]. Consistent with this equivalence, Lopez-Avila stated that the response of the HECD in the halogen mode was roughly proportional to the number of chlorine atoms present [148]. Also, we have found the HECD response, relative to a response standard, to be directly related to the amount of organic chlorine for GC eluates [20]. The proportional relationship allows for chlorinated hydrocarbon determinations using response factor calibration which does not require identical reference

materials for each analyte nor analyte identification [20]. Similarly, Nulton, et al., reported total organic halide concentrations for environmental samples using the HECD and approximated HECD response factors for several toxicants [128].

All the HECD measurements described above require an equivalent HECD response factor for organic chlorine from the measured chlorinated analytes, and therefore reproducible reaction of organic chlorine to HCl prior to HECD conductometry. However, the extent of analyte reduction in HECD catalysis is temperature dependent and affects the HECD response factors. Criteria for HECD reactor temperature selection have been studied, based upon optimum measured conductivities [142, 140, 145, 164, 165], but reaction efficiency has not been well characterized.

This paper presents data on temperature dependencies of analyte reductions in the HECD for chlorinated hydrocarbons. The reactor temperatures required for complete analyte degradation should generally be exceeded in determinations which require equivalent HECD response factors for organic chlorine. Additionally, degradation temperature dependencies could allow for judicious selection of temperatures, perhaps providing discrimination against some analytes and thereby enhancing selectivity [112].

Experimental

Reagents

Chlorinated hydrocarbons were purchased from Aldrich Chemical Company: 1-chlorooctane (1COA, 99% pure), (1,2,3-trichloropropane (TCPrA, 99+% pure), 1,5-dichloropentane (DCPeA, 99% pure), 1-chlorobenzene (CB, 99% pure), 1,2,4-trichlorobenzene (TCB, 99+% pure), hexachlorobutadiene (HCBD, 98% pure) and hexachlorocyclopentadiene (HCCPD, 98% pure). Reference solutions were provided by the U.S. Environmental Protection Agency: 1,2-dichlorobenzene (1,2-DCB, 99.8% pure), 1,3-dichlorobenzene (1,3-DCB, 99+% pure), 1,4-dichlorobenzene (1,4-DCB, 99.9% pure), 2,4,6-trichloroaniline (TCAn, 99% pure) and polychlorinated biphenyl 1016 (PCB 1016). Resi-analyzed grade n-hexane was purchased from J.T. Baker Chemical Co.

Procedures

Solutions of the twelve substances were prepared at concentrations ranging from about 30 µg/mL to 100 µg/mL. Class A volumetric glassware and n-hexane were used for all dilutions.

A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was used with a 2m X 2mm ID glass column, packed with 3% OV-17 on 100/120 Supelcoport. The outlet from the HECD reactor was connected to either the membrane separator or a jet

separator GC-MS interface for a Hewlett-Packard Model 5980A mass spectrometer (GC-reactor-MS). The mass spectrometer used electron impact ionization at 70 eV. Airco grade 4.5 helium was used as the carrier gas at 25 mL/min. Airco grade 4.5 hydrogen with a hydrocarbon trap was used as the HECD reactor gas at 40 mL/min, a typical hydrogen flow rate. The nickel catalyst reactor temperature was varied from 250 ^{o}C to 1000 ^{o}C, the HECD base temperature was 250 ^{o}C and the GC injector temperature was 250 ^{o}C.

A Hewlett-Packard Model 3390A integrator was used to measure total ion chromatogram (TIC) peak areas and retention times. Mass ranges monitored by the TIC were from 50 m/z to 300 m/z except for PCB 1016 which was monitored from 50 m/z to 500 m/z. PCB peak areas included all eluted PCB isomers. A Bell and Howell Model 5-154 Datagraph oscillograph recorded mass spectra.

Results and Discussion

Chlorinated hydrocarbon solutions were injected into the GC-reactor-MS system which contained the membrane separator GC-MS interface. Analytes which were not reduced in the HECD reactor crossed the membrane, were measured by the mass spectrometer and recorded as a total ion chromatogram (figure 11). Polar, low molecular weight degradation products, e.g. HCl, do not readily cross the membrane. As the reactor temperature was increased from 250 ^{o}C to 950 ^{o}C, the TIC peak areas for the analytes are diminished below baseline noise levels (figure 11): no

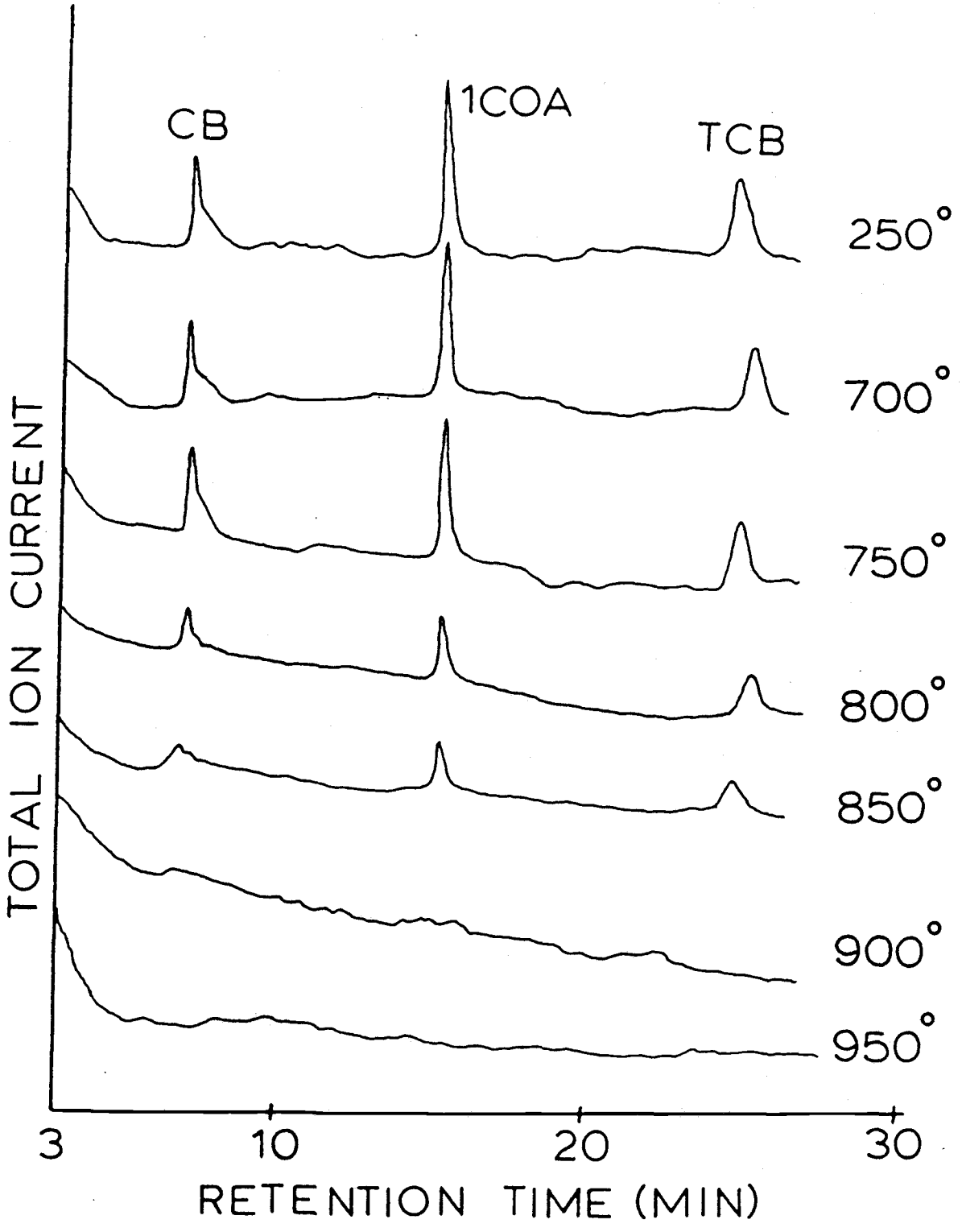

Figure 11. Total ion chromatograms measured by the GC-reactor-MS system at reactor temperatures between 250 °C to 950 °C. The GC temperature program increased from 30 °C to 75 °C at 4 °C/min after a 5 min isothermal period at 30 °C.

reaction occurs at 250 °C. Figure 12 shows the percent analyte reacted, relative to the TIC peak areas at 250 °C, as a function of reactor temperature for the twelve substances: these data are sufficient for selection of temperatures for complete analyte reduction. Several of the chlorinated hydrocarbons were not completely reduced below 950 °C, and their compared reduction yields varied greatly at 800 °C. Thus, HECD response factors are not constant for all chlorinated hydrocarbons at catalysis temperatures lower than 950 °C.

To corroborate these results, the GC-reactor-MS system was also used with a jet separator GC-MS interface. The jet separator allowed HCl as well as other degradation products to pass into the mass spectrometer. Measurements of chlorinated hydrocarbon eluates from the HECD reactor at 950 °C produced mass spectra illustrated by figure 13 after background subtraction. The mass spectra correspond to HCl without the presence of other reduction products at higher masses [158]. Therefore, analyte reduction to HCl is quantitative at 950 °C. This is consistent with the assertion that in the halogen mode HCl and CH_4 result as HECD reactor products for chlorinated hydrocarbons [112]: methane does not give an HECD response under normal operating conditions [112]. Therefore, the HECD response factor for organic chloride is equivalent for these chlorinated hydrocarbons at reactor temperatures exceeding 950 °C since the organic chlorine is quantitatively reduced to HCl.

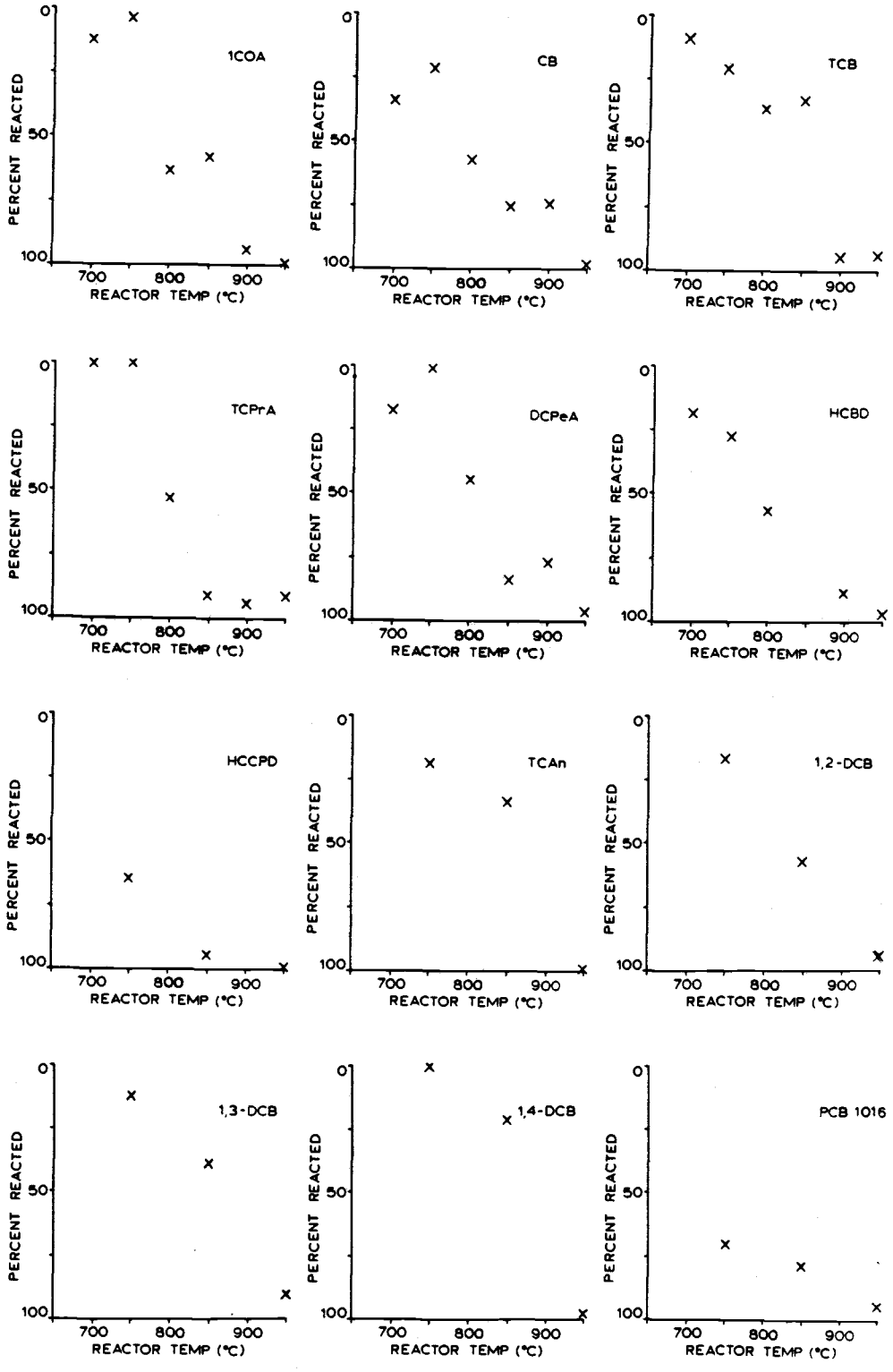

Figure 12. Percent analyte reacted in HECD vs. HECD reactor temperature for chlorinated hydrocarbons.

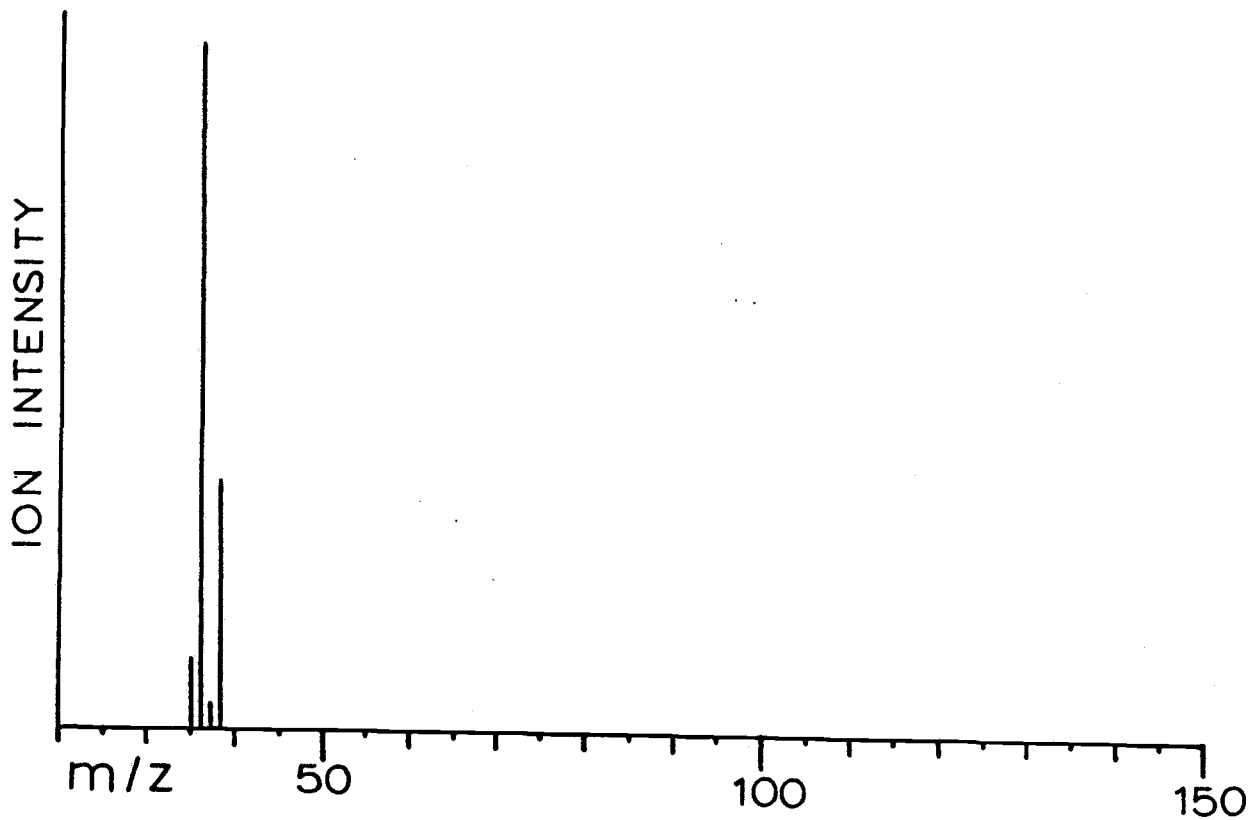

Figure 13. Mass spectrum of HECD reactor effluent after injection of TCPrA.

These data indicate that determinations which require the same HECD response factor for organic chloride from different chlorinated hydrocarbon analytes should use a reactor temperature of at least 950 ^{o}C unless another temperature is properly justified. Other analyte compounds could be evaluated with GC-reactor-MS systems to similarly identify reactor temperatures needed for complete analyte degradation.

V. FLOW OPTIMIZATION FOR THE HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

Introduction

HECD response factors can be influenced by many variables. The HECD reactor temperature affects the HECD response, and reactor temperature selection for RFC has been discussed in Section IV. Also, flow rates for carrier gas, reaction gas and conductivity solvent can affect the HECD response [142, 145, 164].

Carrier gas, usually helium which contains dissolved column eluates, is introduced to the high temperature reactor from the chromatographic column (figure 1). Reaction gas, hydrogen for the halogen mode, is added to the carrier gas prior to exposure to the reactor's the nickel catalyst. Reactor effluents, containing helium, hydrogen and reactor products, mix with n-propanol in the gas-liquid contactor and the gas-liquid separator then isolates the liquid phase from undissolved gases for conductivity measurements in the analytical cell. Flows through these mixing and separation regions of the differential conductivity cell affect the HECD response.

A factorial experiment was conducted to obtain a response surface which estimates affects of carrier gas flow, reaction gas flow and conductivity solvent flow on the HECD response [166]. These three flow variables, or factors [153], were deliberately varied in a controlled fashion and corresponding HECD peak area responses were measured. A second-order multiple regression

model was used to estimate the relationship between the three factors and the response surface [167]. The regression model and Yates' Method of Analysis [153] were used to evaluate the main effects of each factor, i.e., variations of the average response factor as a single factor is varied, and the interaction effects between pairs of different factors [153]. This information allowed optimized flow settings to be estimated for the HECD system such that detector sensitivity could be optimized. This was done for both packed and capillary column systems.

Other variables may also affect the HECD response such as conductivity cell temperature, reactor catalyst integrity, eluate peak shape, solvent background conductance and solvent pH. These background variables [153] were not evaluated in this factorial experiment, but previous work with the HECD has shown these variables to change slowly with time or contribute toward only minor changes in HECD response factors [110, 111]. Including any of these background variables as factors, in addition to the three flow factors, would have markedly increased the number of required experiments [153].

Experimental

Chromatographic instrumentation described in Section III for use of the HECD in the halogen mode with GC, was also used for experiments in this section. A reactor temperature of 950 ^{o}C was used, as recommended in Section IV for chlorinated hydrocarbon analyses. Gas flow rates were measured with a soap bubble meter at

the differential conductance cell exit. Solvent flow rates were measured with a 10 mL graduated cylinder at the same cell outlet. For both flow measurements, a stop watch was used to monitor elapsed time. The vent valve remained closed during all flow measurements.

The following procedure was used to set and monitor the three flow rates:

i) Solvent flow was turned off,

ii) Reactor gas flow was turned off,

iii) Vent valve was closed,

iv) Carrier gas flow was adjusted and measured,

v) Reaction gas flow was adjusted and the carrier gas plus reaction gas flow was measured,

vi) Solvent flow was adjusted and measured.

When a particular flow was changed, only flows which followed in the procedure were reset and remeasured. For example, if the reaction gas flow was changed, then the carrier gas flow was left unchanged and the solvent flow was reset and remeasured.

One μL of a 1-chlorooctane (1COA) standard solution prepared at 59 nmol Cl/mL in n-hexane was repeatedly injected and separated isothermally at 65 ^{o}C for each set of flow conditions evaluated. The 1COA peak area was evaluated from chromatograms obtained for each set of flow conditions defined by the central composite factorial experiment. The baseline noise was always small during these experiments, but largest when both solvent and helium flows were low.

Factorial Experimental Design

Factorial experiments allow the main and interaction effects within an multivariate system to be evaluated. Factorial experiments are efficient since they provide information after fewer experimental trials than normally required by single-factor experiments [166]. However, the number of factors and interactions evaluated must be limited since complete multi-factorial experiments can also require large numbers of experiments. Fractional factorial experiments reduce the number of required trials by neglecting selected high-order interactions [166].

In this study a three level, three-factor experiment was implemented to evaluate effects of the three flow factors on HECD response. The experiment can be pictorially represented by a cube with the center placed at the origin, or base point [156], of a Cartesian coordinate system (figure 14). The X, Y, and Z axes represent the three flow factors, k_1, k_2 and k_3, under evaluation. Each position in the cube defines a combination of the three flow rates, and each position in the cube can also be related to a point on a response surface. The relationship is often estimated by fitting the factorial data with a multiple linear regression to a polynomial function [166]. For these experiments the response surface describes the relationship between the the three flow factors and the 1COA response.

The number of trials required for a complete factorial experiment is Q^k where k factors are evaluated at Q levels [153]. Thus, complete, or 3^k, factorial design for three factors

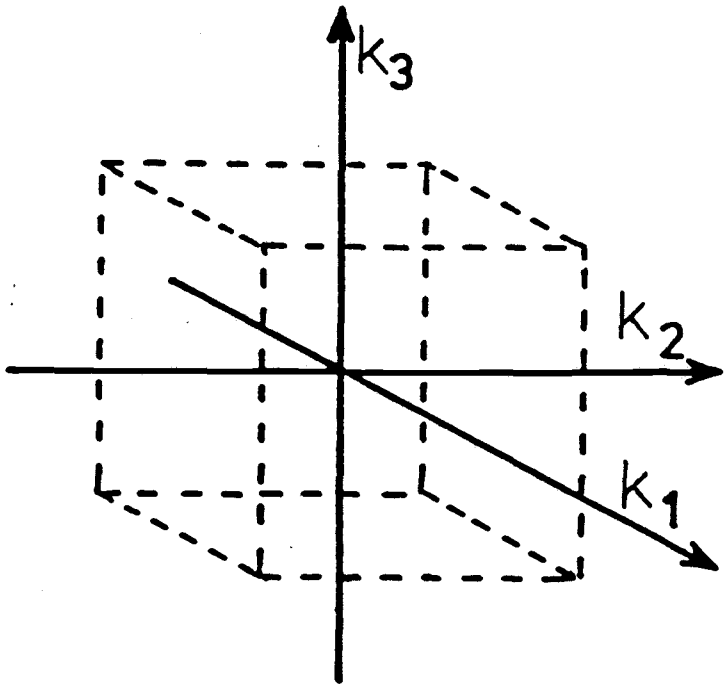

Figure 14. Factorial experimental space for three factors: k_1, x-axis; k_2, y-axis and k_3, z-axis.

would require HECD response measurements for the 27 flow combinations represented by the 27 points on the cube shown in figure 15. The data obtained from a 3^k design may then be modelled by a second-order polynomial with parameters for main effects, two-way interactions and three-way interactions [167]:

$$
\begin{aligned}
y = {} & \beta_0 \\
& \text{main effect terms} \\
& + \beta_1 x_1 + \beta_2 x_1^2 + \beta_3 x_2 + \beta_4 x_2^2 + \beta_5 x_3 + \beta_6 x_3^2 \\
& \text{two-way interaction terms} \\
& + \beta_7 x_1 x_2 + \beta_8 x_{13} + \beta_9 x_2 x_3 + \beta_{10} x_1 x_2^2 + \beta_{11} x_1 x_3^2 \\
& + \beta_{12} x_2 x_1^2 + \beta_{13} x_2 x_3^2 + \beta_{14} x_3 x_1^2 + \beta_{15} x_3 x_2^2 \\
& \text{three-way interaction terms} \\
& + \beta_{16} x_1 x_2 x_3 + \beta_{17} x_1 x_2 x_3^2 + \beta_{18} x_1 x_2^2 x_3 + \beta_{19} x_1^2 x_2 x_3 \\
& + \beta_{20} x_1 x_2^2 x_3^2 + \beta_{21} x_1^2 x_2^2 x_3 + \beta_{22} x_1^2 x_2 x_3^2 \\
& + \beta_{23} x_1^2 x_2^2 x_3^2 \\
& \text{error term} \\
& + e
\end{aligned}
\tag{19}
$$

for which y estimates the response surface to factors x_1, x_2 and x_3.

A less complete but often sufficient factorial experiment may be selected. For example, the central composite $(2^k + 2k + 1)$ factorial design requires only 15 HECD response factor measurements

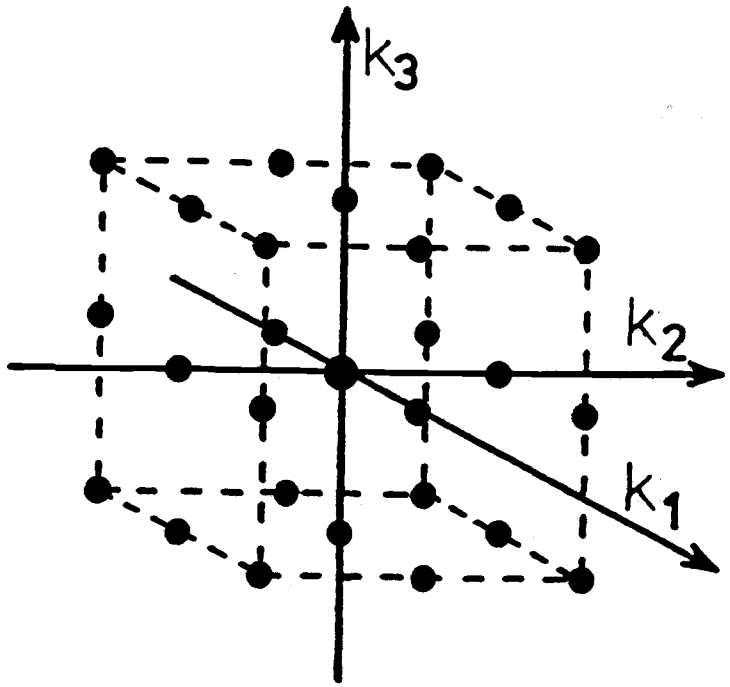

Figure 15. A three factor, 3^k factorial experimental space. Dots represent the 27 positions at which measurements are required for a complete factorial experiment.

at the flow combinations represented in figure 16 [167]. Central composite data can be fit to a second order polynomial which includes only parameters for the main and second order two-way interaction effects [168]:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_1^2 + \beta_3 x_2 + \beta_4 x_2^2 + \beta_5 x_3 + \beta_6 x_3^2 + \beta_7 x_1 x_2 + \beta_8 x_1 x_3 + \beta_9 x_2 x_3 + e \qquad (20)$$

Again, y estimates the response surface to factors x_1, x_2 and x_3. The central composite design is suggested for fitting factorial data by multiple regression since fewer trials are required [166, 156, 167-170]: the central composite design uses a minimum of $(Q-1)^k + (Q-1)^k + 1$ experiments compared to the Q^k experiments required for a complete factorial experiment [167].

Multivariate Evaluation of the Effects of Reaction Gas, Carrier Gas, and Conductivity Solvent Flow Rates on the HECD Response by a Central Composite Factorial Experiment

The effects of helium carrier gas, hydrogen reaction gas, and n-propanol conductivity solvent flow rates on the HECD response in the halogen mode were evaluated with a three level, three factor, factorial experiment (figure 14). In this experiment, the three factors were reaction gas flow rate, k_1, carrier gas flow rate, k_2, and conductivity solvent flow rate, k_3. The HECD response was the 1COA peak area obtained from HECD chromatograms.

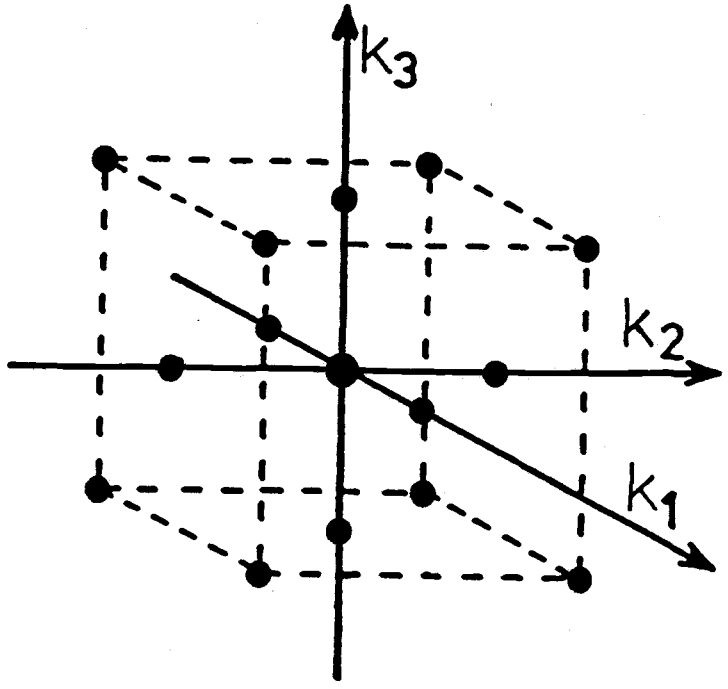

Figure 16. A three factor, $2^k + 2k + 1$ factorial experimental space. Dots represent the 15 positions at which measurements are required for a central composite factorial experiment.

The central composite design was chosen to evaluate the HECD response surface to the three flows in the halogen mode in order to minimize the number of trials. The second-order polynomial, equation 20, was selected for modeling factorial data by multiple regression; this selection was based on limited single-factor flow data in the literature related to the HECD. For example, Galoux, Damme, Bernes and Potvin evaluated hydrogen flow rates in the nitrogen mode [142]; Wilson and Cochrane evaluated hydrogen flow and conductivity solvent flow in the nitrogen mode [164]; and Gluck evaluated conductivity solvent flow rate in the sulfur mode [145]. Those authors have suggested that HECD response generally increases as hydrogen flow rate increases and decreases as conductivity solvent flow rate increases in a second order fashion without major inflection points. Personal experience with the HECD in the halogen mode suggested the same trends. High-order interaction effects were not evaluated for the HECD in the halogen mode using the second order polynomial in equation 20 since the number of required experiments would have been large, requiring a complete factorial experiment.

Flow ranges which are reasonable for the HECD system established the boundaries of the cube (Table 4). Carrier gas flow is limited since analyte elution is severely retarded at very low flow rates, less than 10 mL/min, but analytes are lost during the venting procedure at very high flow rates, greater than 40 mL/min. Conductivity solvent flow is limited by the useful range of the delivery pump since at low flow rates, less than 0.2 mL/min, the system becomes erratic, and the upper flow rate limit is about

Table 4. Target HECD flow boundaries established for the three factor experiment, defining the experimental space boundaries. Actual HECD flow boundaries are shown in parentheses.

Factors (mL/min)		Level (Three Level Experiment)		
		Q_0: Low Level	Q_b: Base Level	Q_1: High Level
k_1	hydrogen gas flow (reaction gas)	10 (12.7)	30 (30.0)	50 (51.2)
k_2	helium gas flow (carrier gas)	10 (12.3)	30 (35.8)	50 (55.8)
k_3	solvent flow (conductivity solvent)	0.2 (0.3)	1.6 (1.4)	3.0 (2.7)

4 mL/min. Reaction gas flow is also limited since the gas/liquid flow ratio is important in the gas-liquid contactor and separator. Recommended gas/liquid flow ratios are about 100:1 [110].

Cochran and Cox recommend that for a three factor, three level, second order, central composite design the system should be evaluated at points corresponding to the eight vertices of the cube, the centers of the six faces of the cube and the base point [166]. These authors also recommend that replicate measurements be obtained for the base point. As a result, eight chromatograms were developed with the flow conditions set as defined by the vertices of the cube, and six chromatograms were developed as defined by the centers of the faces of the cube. The flow conditions were also set as defined by the base point, for which five chromatograms were obtained. The sequence used to obtain the 19 chromatograms is shown in Table 5, which displays the values for each factor and the 1COA peak areas from each experiment. The experimental sequence was not completely randomized due to practical limitations in resetting the flow rates precisely.

The data analysis computer program, listed in Appendix D, was used to fit the factorial data to the multiple linear regression function. The expected 1COA peak area responses, as estimated by the polynomial regression function, and regression residuals are listed in Table 5. Regression parameters resulting from fitting equation 20 to the factorial data are shown in Table 6, which also includes confidence intervals based on the student's t-statistic for each of the ten regression parameters. The 90% confidence intervals were calculated from the diagonal elements of the

Table 5. Factor combinations, observed 1COA peak area response. Expected 1COA peak areas, and 1COA peak area residuals. Chromatograms are listed in the experimental sequence used.

Chrom. Number	Flow Rate (mL/min)			1COA Peak Area (area units)		
	Hydrogen	Helium	Solvent			
	k_1	k_2	k_3	Observed Area	Expected Area	Area Residuals
1	12.7	11.5	0.31	250	291	-41
2	12.7	11.5	2.7	40	19	22
3	12.7	55.7	0.31	481	481	0.02
4	12.7	55.7	2.7	59	59	0.06
5	49.9	13.0	0.31	409	406	3.0
6	49.9	13.0	2.7	52	61	-8.9
7	49.9	56.5	0.31	491	515	-24
8	49.9	56.5	2.7	57	23	35
9	28.9	36.1	1.4	123	136	-14
10	28.9	36.1	1.4	113	136	-23
11	28.9	36.1	1.4	130	136	-6.4
12	28.9	36.1	1.4	134	136	-2.1
13	28.9	36.1	1.4	130	136	-5.8
14	28.9	36.1	3.0	61	95	-34
15	28.9	36.1	0.31	518	450	68
16	12.9	34.7	1.4	128	107	21
17	56.2	34.7	1.4	141	144	-3.2
18	29.2	54.7	1.4	149	160	-11
19	29.2	12.3	1.4	101	76	25

Table 6. Multiple regression parameters for the ICOA peak area response surface to hydrogen, helium and solvent flow rates. 90% confidence interval estimates for the individual regression parameters are included [153].

Regression Parameter	Parameter Value	Estimated 90% Confidence Interval for Parameters	Parameter Description		
			Effect Type	Factors	Parameter Order
β_0	2.7×10^2	1.0×10^2	----	----	intercept
β_1	5.6	5.1	main	hydrogen	first
β_2	-2.9×10^{-2}	7.0×10^{-2}		flow	second
β_3	7.3	4.3	main	helium	first
β_4	-2.9×10^{-2}	6.0×10^{-2}		flow	second
β_5	-3.8×10^2	0.7×10^2	main	solvent	first
β_6	97.	18.		flow	second
β_7	-4.7×10^{-2}	4.4×10^{-2}	inter-	hyd. & hel.	second
β_8	-0.76	0.80	action	hyd. & sol.	second
β_9	1.4	0.7		hel. & sol.	second

inverted regression matrix and parameter standard deviations, which were calculated from the sum of squared residual values [153].

The regression parameters indicate that solvent flow has the largest effect among the three factors on the HECD response. The first and second order regression parameters for the main-effect of solvent flow on the HECD response are much larger than for any other effect. The hydrogen and helium flow factors yield smaller main-effect parameters than solvent flow, and the first and second main-effect parameters are both similar for the two gas flow factors. This suggests that the total gas flow rate through the HECD is more important for HECD response evaluation than the individual flow rates of hydrogen or helium within the flow boundaries evaluated in this experiment. The 90% confidence intervals indicate that the second-order parameters for hydrogen and helium flow, and the three interaction-effect terms all are small when compared to other parameters.

The polynomial model was evaluated to demonstrate effects of a single flow on the HECD response while the remaining two flows were held constant at base point values. As suspected, if solvent flow is increased while carrier and reaction gas flows remain constant, then the HECD response is actually reduced (figure 17). For example, a conductivity solvent flow of 0.2 mL/min yields about ten times the HECD response found with a flow of 2.5 mL/min.

The HECD response increases as either reaction gas or carrier gas flows are increased. Increasing helium flow from 10 mL/min to 50 mL/min produces a 120% increase in the HECD response with the other two factors held constant at base point values (figure 18).

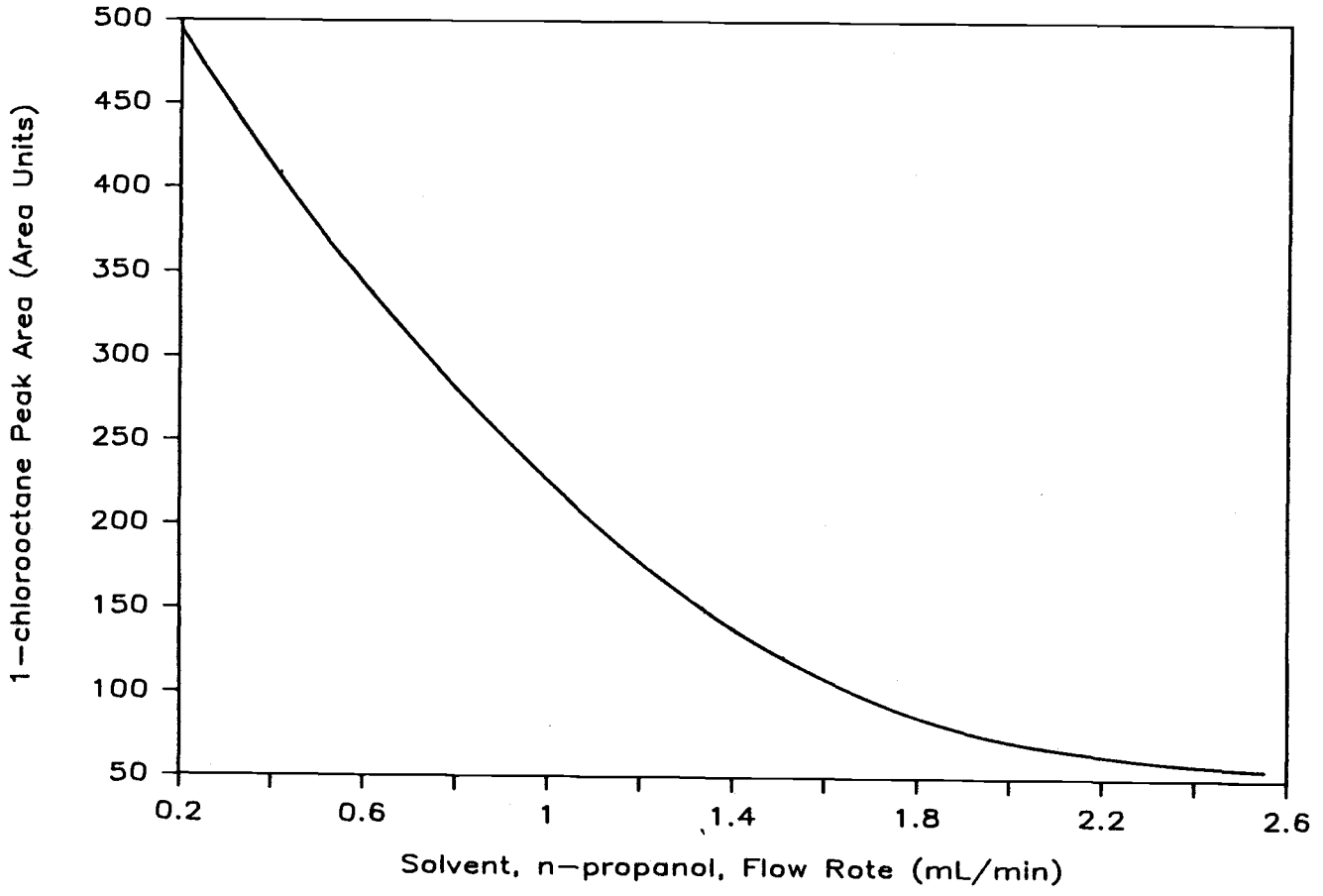

Figure 17. Effect of HECD solvent flow on 1COA peak area, hydrogen flow = 28.9 mL/min. helium flow = 36.1 mL/min.

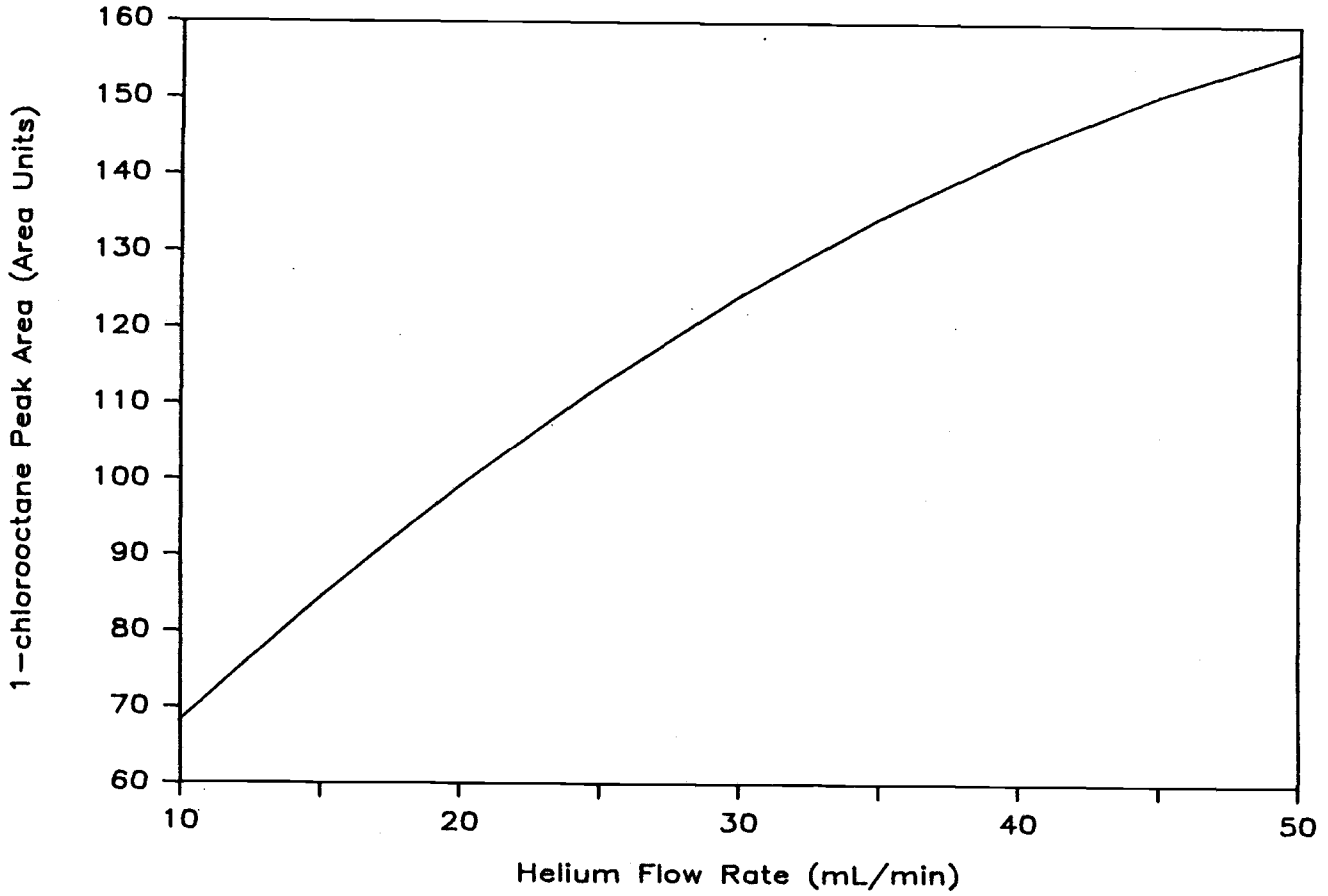

Figure 18. Effect of HECD helium carrier gas flow on peak area, hydrogen flow = 28.9 mL/min, solvent flow = 1.4 mL/min.

Similarly, a hydrogen flow increase over the same flow ranges yields a 43% increase in the HECD response (figure 19). However, since the helium flow at the base point is larger than the hydrogen flow at the base point, different total gas flow rates are being compared. Evaluation of the hydrogen flow rates from 10 mL/min to 50 mL/min with the helium flow constant at 28.9 mL/min, and solvent flow constant at 1.4 mL/min, shows an HECD response increase of 65% (figure 20).

When the parameter 90% confidence intervals are considered (Table 6), figures 18 and 20 illustrate similar relationships between helium or hydrogen flow and the HECD response. A total gas flow rate seems to yield approximately the same HECD response even if the ratio of hydrogen to helium flow changes. Thus, hydrogen gas is probably only needed in small amounts as a reagent. Moreover, the increase in the HECD response as gas flow increases may reflect changes in mixing dynamics within the gas-liquid contactor and gas-liquid separator.

Evaluation of the Main Effects and Interaction Effects of Reaction Gas, Carrier Gas and Conductivity Solvent Flow Rates on the HECD Response by Yates' Method

Yates' method for analysis of factorial experiment data was also applied to the evaluation of effects of the three flow factors on HECD response [153]. Yate's method utilizes simple calculations to quickly estimate the main and interaction effects, however, the method is restricted to two level experiments. Thus, only the

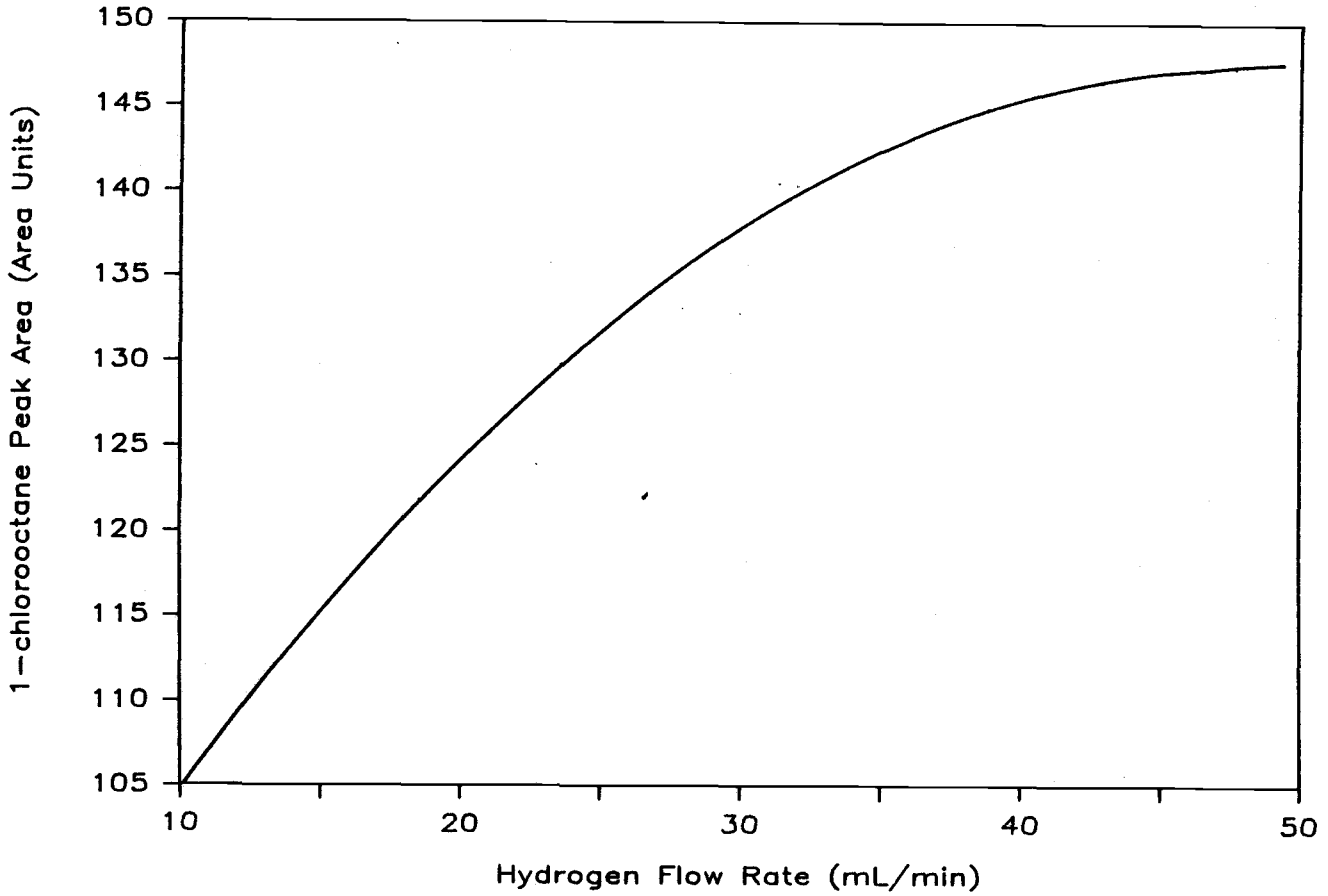

Figure 19. Effect of HECD hydrogen flow on 1COA peak area, helium flow = 36.1 mL/min, solvent flow = 1.4 mL/min.

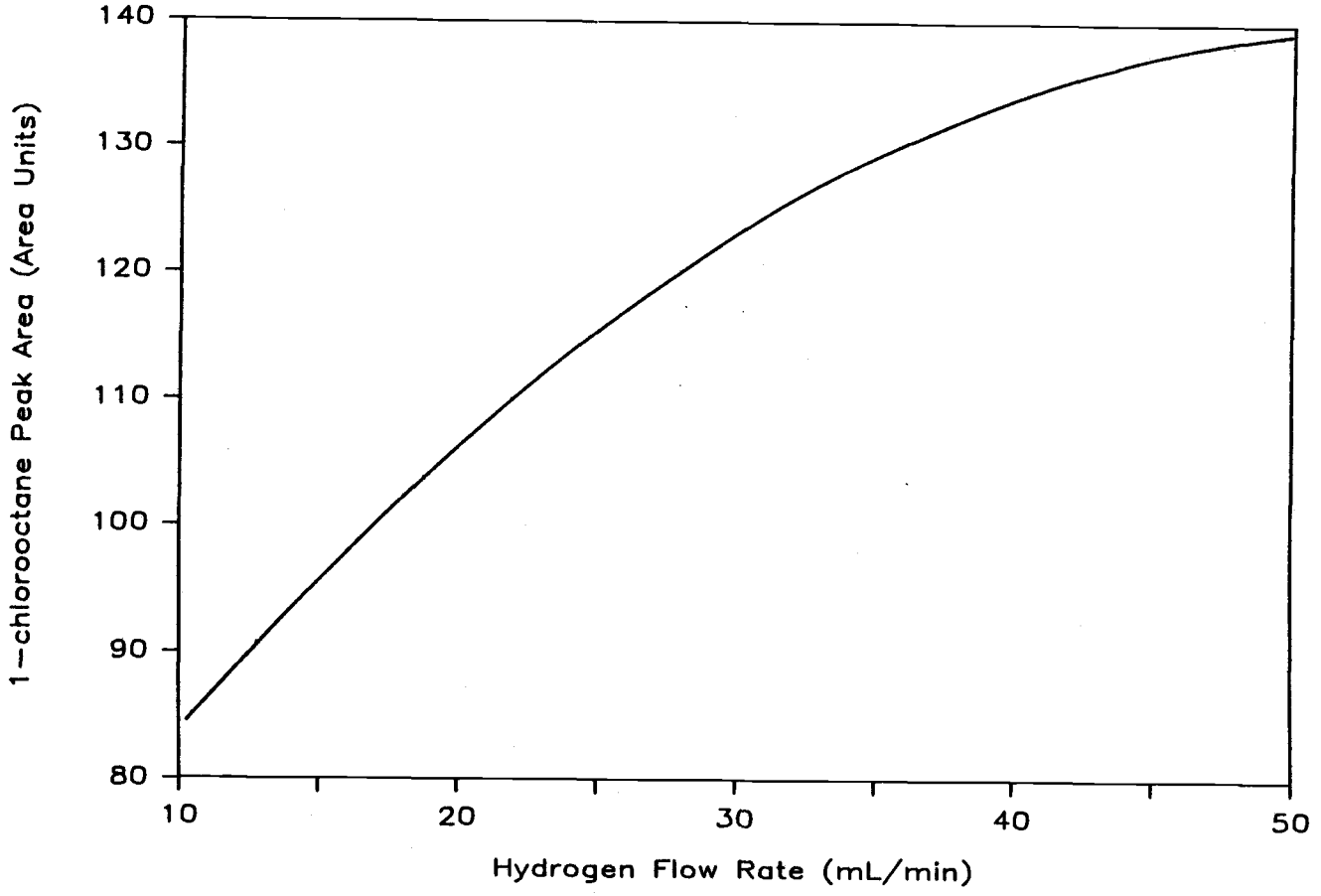

Figure 20. Effect of HECD hydrogen flow on 1COA peak area, helium flow = 28.9 mL/min, solvent flow = 1.4 mL/min.

eight chromatograms, corresponding to the eight vertices of the experimental cube in figure 16, were used (Table 7). The resulting estimates of Yates' effects suggest similar trends as were suggested by the multiple regression analyses described above.

The 90% confidence interval calculated for Yates' method in Table 7 indicates that only three effects are different from zero at the 90% confidence level: the main effects of solvent and helium flows and the interaction effect between solvent and helium flows [153]. These confidence intervals are based upon the student's t-statistic. The estimate of the main effect of solvent flow on the HECD response is much larger than the main effect for hydrogen or helium flows as observed in the multiple regression evaluation. However, Yates' method suggests that the interaction effect between helium and solvent flows is much more significant than estimated by the multiple regression evaluation.

Yates' method consists of quick and simple calculations which allow a prompt evaluation of factorial experimental data. However, with the aid of computers, the multiple regression evaluation can also be done quickly. Yates' method is a two level evaluation which does not consider second order relationships which may exist between the individual factors and the HECD response. The second order relationship between solvent flow and the HECD response is evident from the multiple regression parameters and previous work [145].

Table 7. Two level evaluation of effects of the three flow factors on 1COA peak area response by Yates' Method. The eight experiments used for this evaluation correspond to the vertices of a three-factor central composite experimental space [153].

Factors			1COA Peak Area (area units)	Column 3 (area units)	Column 4 (area units)	Column 5 (area units)	Effects on 1COA Peak Area (area units)	
k_1	k_2	k_3						
Q_0	Q_0	Q_0	250	660	1632	1843	460	
Q_1	Q_0	Q_0	409	972	210	180	45	main, k_1
Q_0	Q_1	Q_0	481	93	169	336	84	main, k_2
Q_1	Q_1	Q_0	491	117	10	-163	-40	interaction, k_1 & k_2
Q_0	Q_0	Q_1	40	159	312	-1421	-355	main, k_3
Q_1	Q_0	Q_1	52	10	23	-159	-40	interaction, k_1 & k_3
Q_0	Q_1	Q_1	59	12	-149	-288	-72	interaction, k_2 & k_3
Q_1	Q_1	Q_1	57	-2	-14	135	33	interaction, k_1 & k_2 & k_3

s = 8.4 -- obtained from five replicate chromatograms at base position.
w = 50 -- 90% confidence interval based upon student's t-statistic.

Flow Conditions for Optimum HECD Response with Packed GC Columns

For a packed column HECD system, flow conditions were chosen to provide an optimum HECD response to organochlorine (Table 8). Experiments presented in Section III allowed selection of a reactor temperature above 950 °C to assure complete analyte reduction within the reactor during RFC analyses. A solvent flow rate of 0.5 mL/min provides an enhanced HECD response over higher flows but doesn't introduce significant pump noise into the system. A solvent flow of 0.2 mL/min would further increase HECD response but could increase noise, jeopardizing measurements of analytes near the limit of detection limit.

A hydrogen reaction gas flow rate of 50 mL/min was chosen, which provides the largest HECD response according to the experimental results described above. However, the carrier gas flow affects resolution and retention times in addition to the HECD response. Furthermore, experimental results described above suggest that the HECD response mainly changes with total gas flow. Thus, carrier gas flow should be optimized for resolution and reaction gas flow increased to raise the total gas flow if the HECD response needs to be further enhanced. A helium carrier gas flow rate of 20 mL/min is used for the packed column HECD system.

Figures 21, 22 and 23 illustrate changes in HECD response, based upon the calculated response surface, as single factors are changed while the other flow factors remain constant at the selected optimum flow rates. The effect of solvent, helium and

Table 8. Flow conditions for optimum HECD response and the practical optimum flow conditions for the HECD with packed columns.

Factors		Flow Rate (mL/min)	
		Optimum HECD Response	Practical Optimum Flows
Hydrogen flow	k_1	50	50
Helium flow	k_2	50	20
Solvent	k_3	0.2	0.5

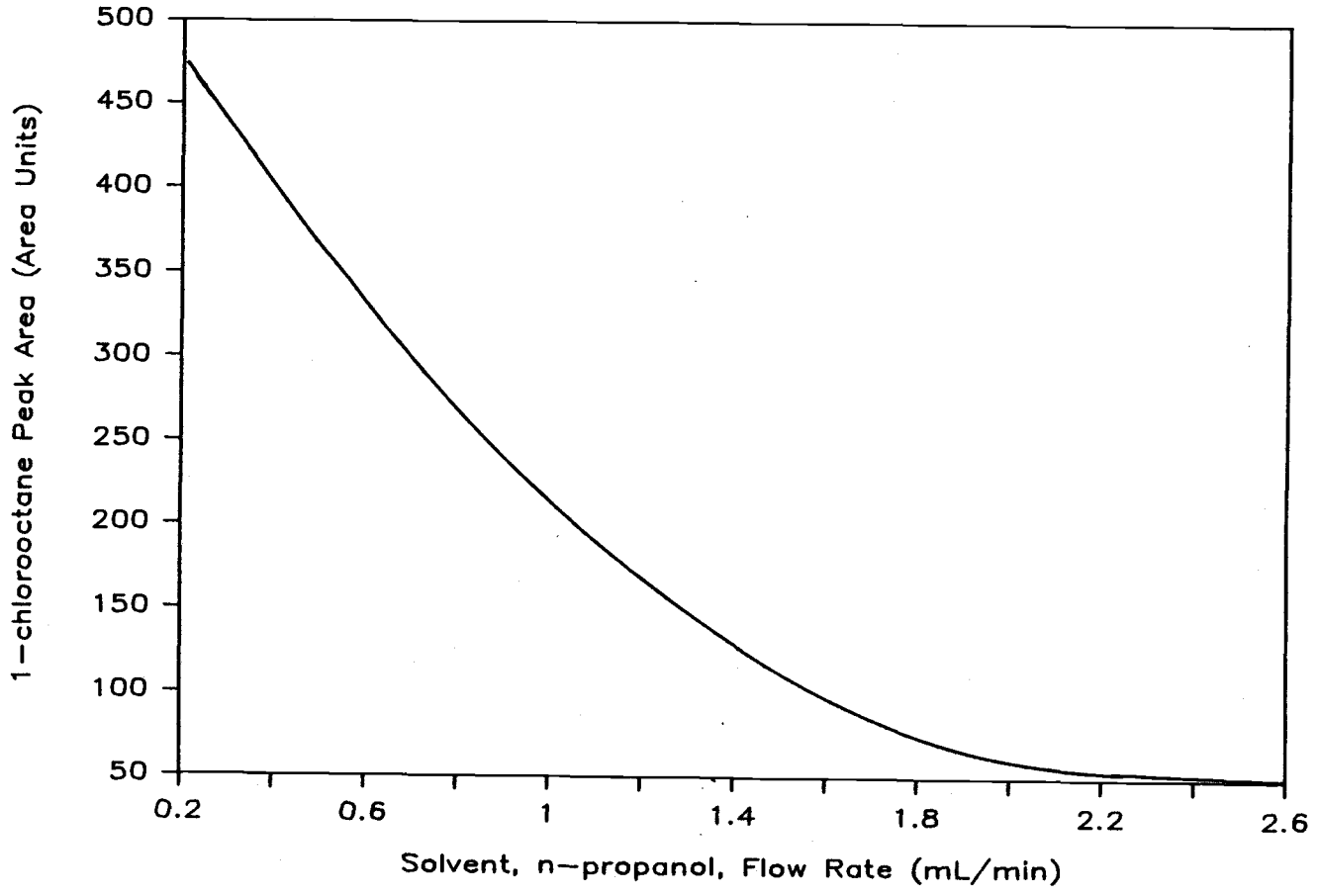

Figure 21. Effect of HECD solvent flow on 1COA peak area, hydrogen flow = 50 mL/min, helium flow = 20 mL/min.

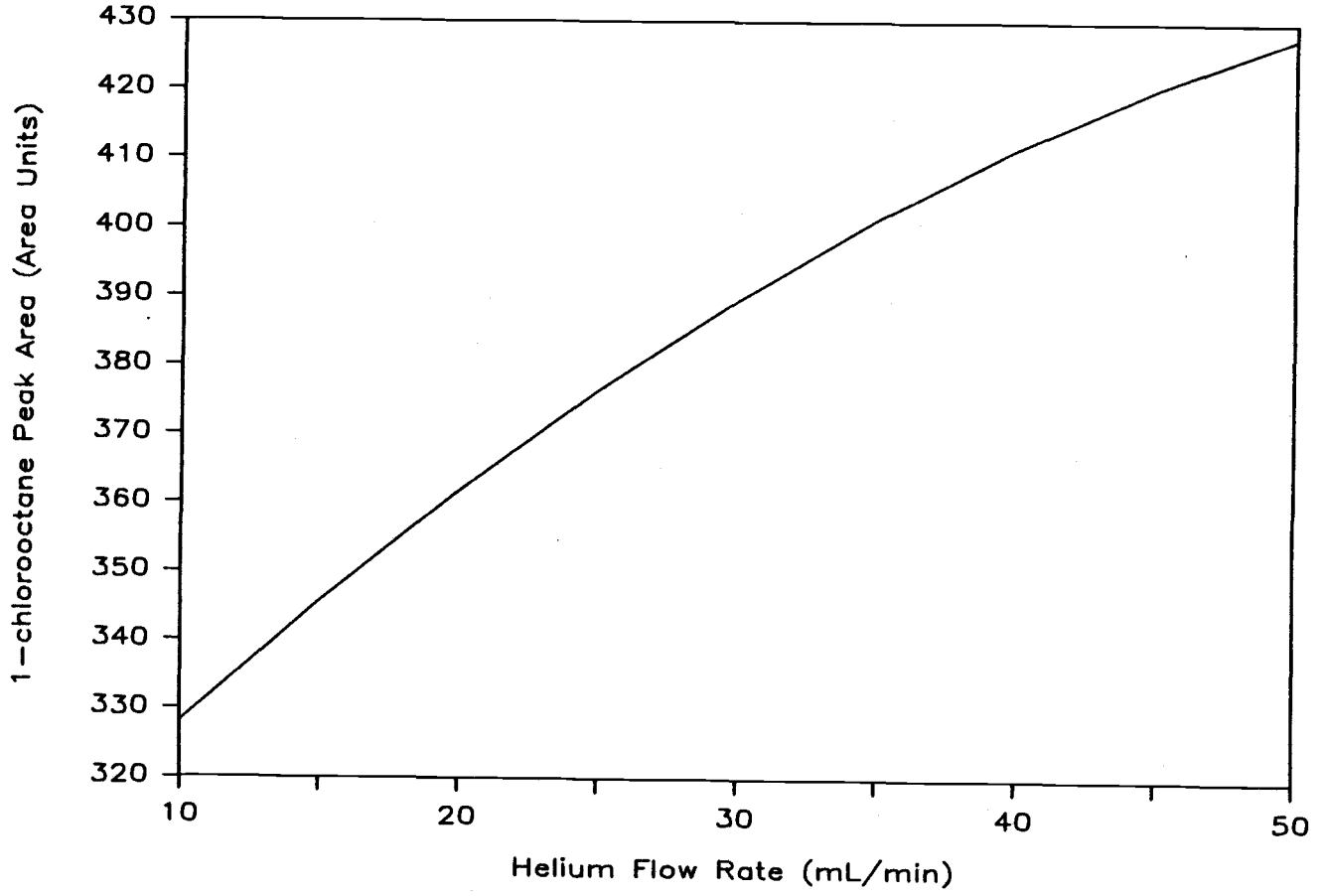

Figure 22. Effect of HECD helium, carrier gas flow on 1COA peak area, hydrogen flow = 50 mL/min, solvent flow = 0.5 mL/min.

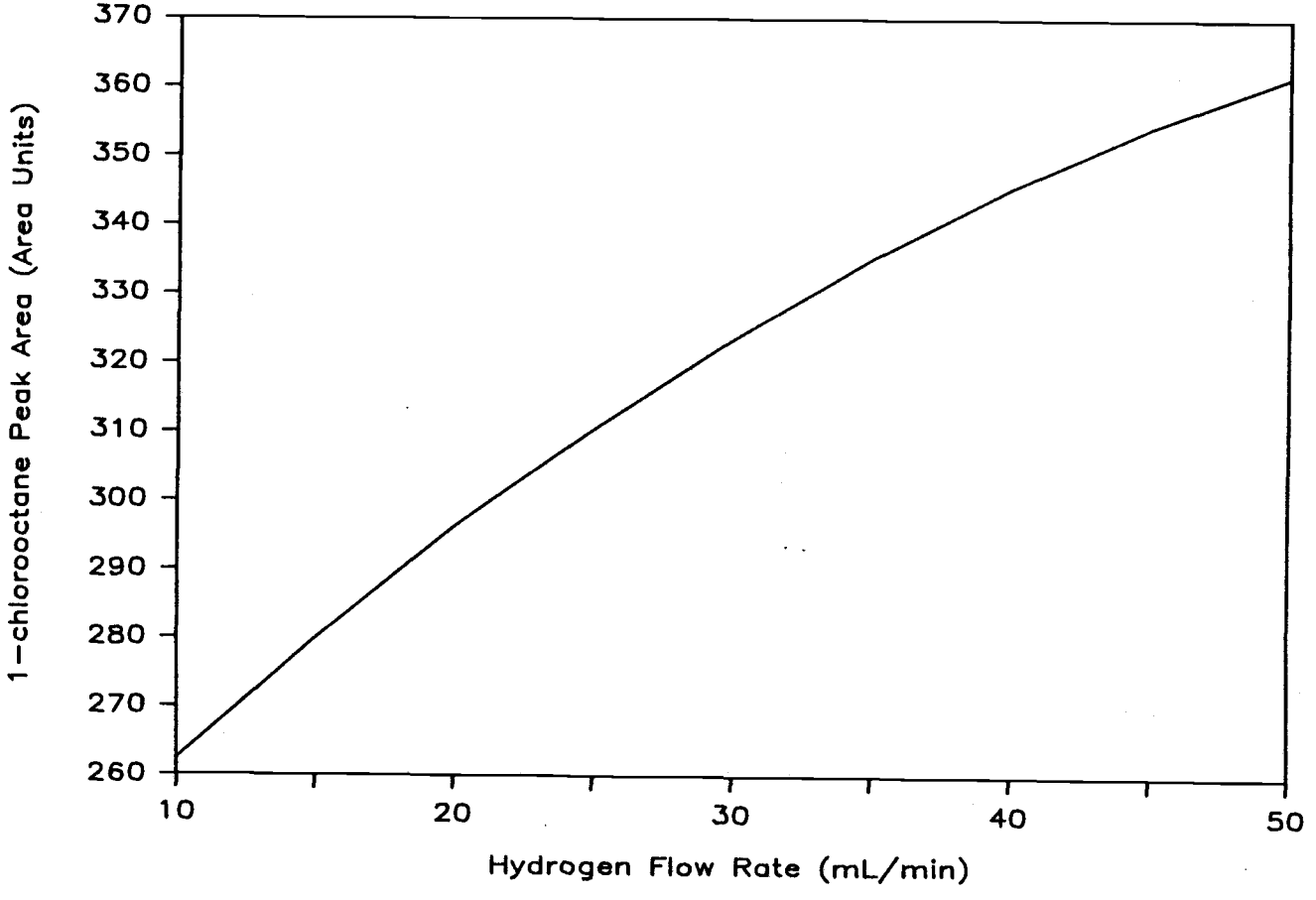

Figure 23. Effect of HECD hydrogen flow on 1COA peak area, helium flow = 20 mL/min, solvent flow = 0.5 mL/min.

hydrogen flows on the HECD response near the optimization point are shown in figures 21, 22 and 23, respectively.

VI. CONSTANT FLOW REQUIREMENTS IN THE HALL ELECTROLYTIC CONDUCTIVITY DETECTOR DURING TEMPERATURE PROGRAMMING

Introduction

Sensitivities for concentration-dependent GC detectors have been related to gas flow through these detectors [171]. The HECD is a concentration-dependent detector since the differential conductance signal is related to the HCl concentration in the conductivity solvent within the detector (Section III). Carrier gas flow remains constant during isothermal separations but may decrease dramatically during temperature programmed separations [171] (figure 24). Experiments from Section V reveal that the HECD response changes when helium carrier gas flow is changed (figure 18). Consequently, as carrier gas flow decreases during a temperature programmed separation, the HECD response factor as measured from the response standard may not remain constant for analytes which elute in the same chromatogram at different temperatures. Thus, flow fluctuations may introduce significant errors when response factor calibration is used for analyte determinations because RFC requires the response factor for the simple measured species to remain constant during the measurement interval. Therefore, implementing a system which maintains constant flow through the HECD, even during temperature programming, is necessary for RFC determinations.

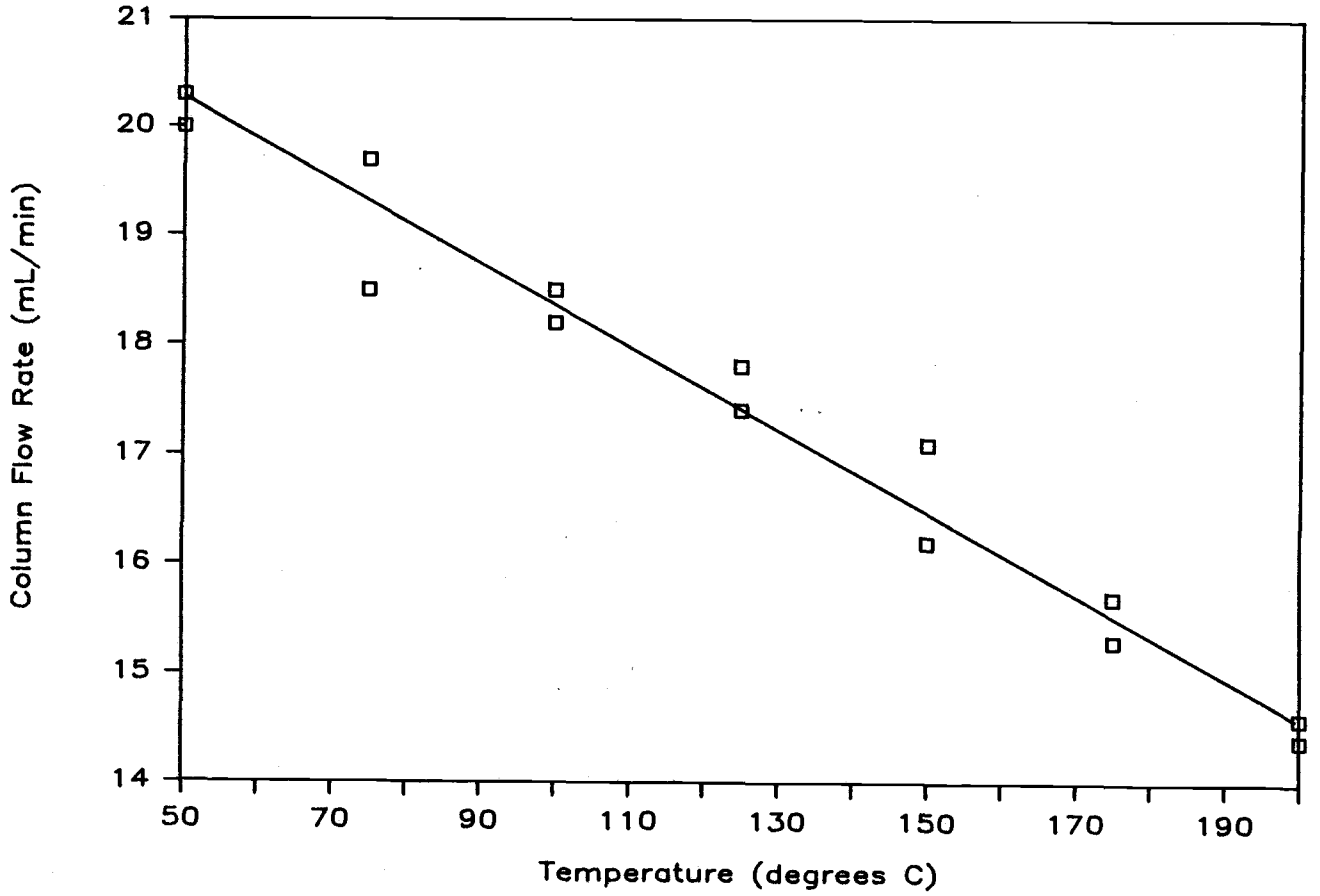

Figure 24. Mass flow rate changes in a packed, 2m x 2mm ID, GC column during temperature programming.

Two different procedures have been utilized in this research to maintain constant gas flow through the HECD during temperature programming. The first system uses packed GC columns with a microcomputer controlled flow adjustment system, utilizing mass flow feedback control. The other technique employs capillary GC columns which use carrier gas flow rates which are low relative to total HECD flow. Thus, carrier gas flow changes in the capillary column, due to temperature programming, will not introduce significant changes in the total HECD flow.

Flow programming in GC utilizing flow control has been reported in the literature [171-177]. Usually these systems employ flow control to exponentially increase column flow during a separation, sometimes during a concurrent temperature program. Wicar has addressed problems of decreasing column flow rates during temperature programming for concentration-dependent GC detectors e.g. the thermal conductivity detector [178, 179]. Along these lines, Dodo, Hawkes and Thomas developed a mass-flow control system for optimized flow programming for temperature programmed GC [171]. Their system has been modified for this research and used for maintaining constant column flow during temperature programming for RFC determinations of chlorinated hydrocarbons.

Experimental

Chromatographic instrumentation described in Section III for use of the HECD in the halogen mode was also used in experiments described here. A flow control system, described below, was

attached to the Tracor 560 gas chromatograph, equipped with a Tracor 700A Hall Electrolytic Conductivity Detector, to maintain constant helium carrier gas flow rates at about 20 mL/min. Hydrogen reaction gas flow rates of 50 mL/min and n-propanol conductivity solvent flow rates of 0.5 mL/min were used based on results described in Section V above. A reactor temperature of 950 ^{o}C was selected as recommended in Section IV for the determination of chlorinated hydrocarbons by RFC.

The flow control system (figure 25) included a Kurz Model 1541 mass-flow meter, a Rockwell AIM 65 microcomputer, a Porter VCD-1000 flow control valve, a Warner Electric Clutch and Brake Co. SM-024-0018 stepper motor and digital electronics based upon a National Semiconductor ADC-0817 analog-to-digital converter [180]. The computer compared the measured mass flow values (FR) with an operator selected mass flow value. This difference is then minimized via the computer by iterative adjustment of the stepper motor, which opens or closes the flow control valve. Comparisons of FR and the desired flow value are repeated throughout each elution, with adjustments of the flow control valve made in response to nonzero differences between FR and the selected set-point. The time constant for the system's response was 3.4 sec.

Constant Flow in the HECD with Packed Columns

The flow control system maintained constant helium carrier gas mass flow within 3% (RSD) of the set volumetric flow, 20 mL/min,

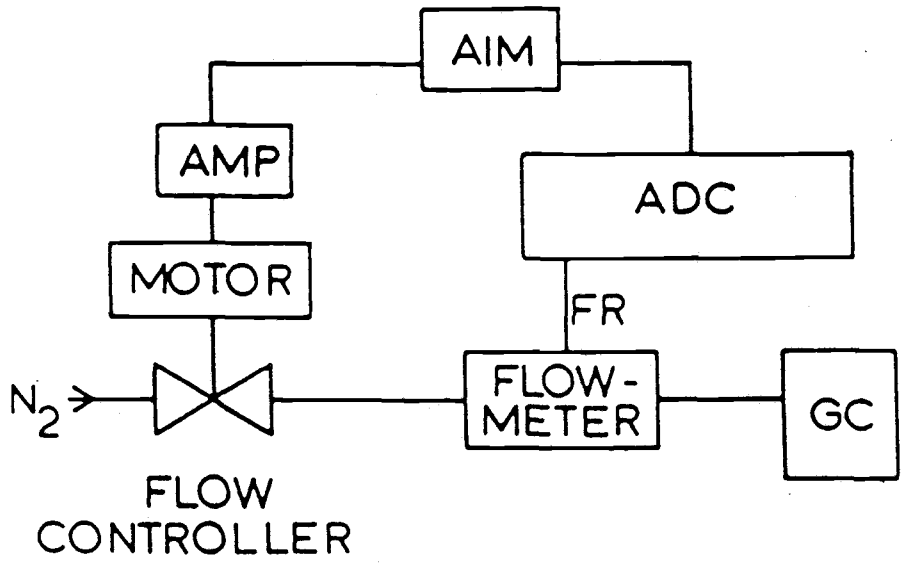

Figure 25. The carrier gas flow control system for packed columns [180].

during temperature programming from 50 °C to 250 °C (figure 26). This flow fluctuation corresponds to variations of the HECD response factor within 2% for the above temperature program (figure 18). However, in the absence of flow control the carrier gas flow rate is reduced by 30%, 25 mL/min to 17.5 mL/min, during the same temperature program (figure 26). Consequently, the 30% flow rate reduction may change the HECD response by 18% during this temperature program (figure 18).

The carrier gas flow control system was utilized for chlorinated hydrocarbon determinations by RFC with a packed GC column and the HECD. A calibration curve for chlorinated hydrocarbons and a 1COA response standard was developed using constant carrier gas flow. This calibration curve was not significantly different from the curve obtained in the absence of flow control, as discussed in Section IIIb. The calibration curve similarity probably results from the short temperature programs, spanning only 40 °C, used for developing the calibration curves. That is, the temperature programs from 30 °C to 70 °C would produce only a 1 mL/min flow change in the absence of flow control, according to figure 26. However, the flow control system only maintains constant flow within 0.6 mL/min, or 3% RSD. Thus, for short temperature programs, over ranges less than 50 °C, this carrier gas flow control system is not expected to provide observable improvement for RFC determinations. However, these small flow fluctuations, less than 1 mL/min, could introduce as much as 3% error in the HECD response as measured via the response standard (figure 18).

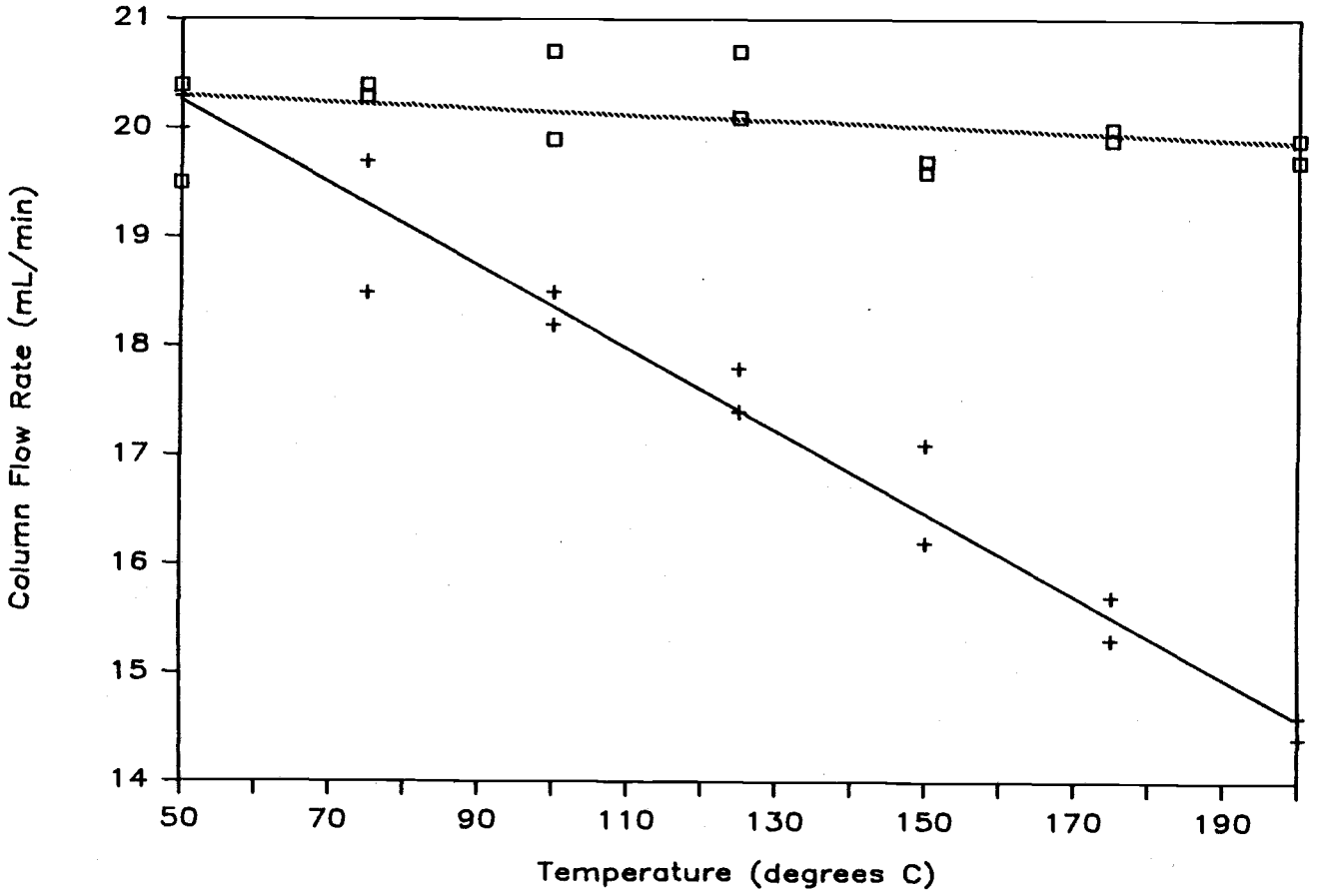

Figure 26. Mass flow rate changes in a packed, 2m x 2mm ID, GC column. (⋯⋯) during temperature programming with the flow control system. (——) normal temperature programming in the absence of flow control.

Constant Flow in the HECD with Capillary Columns

Packed columns are often replaced in gas chromatography by capillary columns to enhance resolution and separation ability. Capillary columns provide an additional advantage with the HECD since carrier gas flow control is not required during temperature programming in order to maintain effective constant flow in the HECD.

The hydrogen carrier gas flow rate in a 30 m X 0.315 mm ID capillary column is typically set to about 1 mL/min with the oven isothermal at 100 ^{o}C. During a temperature program, the capillary column carrier gas flow will decrease, as is observed with a packed column [5, 181]. However, hydrogen make-up and reaction gases are introduced to the column effluent prior to the HECD at a combined flow rate of about 60 mL/min. Thus, even a 50% change of hydrogen flow in the capillary column, i.e. 0.5 mL/min, will produce less than a 1% change in total flow through the HECD. Correspondingly, a 1% reduction in hydrogen flow through the HECD results in an HECD response change of less than 0.5% (figure 20). Thus, errors in HECD response factor measurement, via the response standard, due to carrier gas flow changes are even smaller for capillary columns than for packed columns with constant flow control.

Using capillary columns to maintain constant flow through the HECD is much simpler than implementing the flow control systems necessary for packed columns. In addition, the capillary column

provides enhanced resolution which is welcomed when samples contain many eluates from a complex sample matrix. The HECD was designed primarily for packed GC columns, but adaptation of the HECD for capillary columns is feasible, as presented in Section VII.

VII. ADAPTATION OF THE TRACOR MODEL 700A HALL ELECTROLYTIC CONDUCTIVITY DETECTOR FOR CAPILLARY COLUMNS

Introduction

Capillary columns are often preferred over packed column systems when analytes are to be separated from complex matrices. The higher resolution of capillary columns may substantially reduce the need for lengthy sample preparation procedures. The advent of fused silica capillary columns has resolved many problems associated with earlier glass capillary columns. Recently, the development of robust and durable "bonded phase" or cross-linked fused silica capillary columns has dramatically increased the popularity of capillary GC.

Some of the commonly used detectors in gas chromatography have been redesigned for use with capillary systems. The low capillary flow rates, ca. 1 mL/min, as compared to greater than 20 mL/min for packed columns, and their narrow eluate band-widths have required smaller detector cell volumes, reduced dead-space and the introduction of make-up gas.

The Tracor Hall Electrolytic Conductivity Detector has not been redesigned for optimal use with capillary columns. However, RFC analyses of polychlorinated biphenyls, presented in Section VIII, require high resolution capillary GC separations, which more effectively resolve individual PCB isomers. The HECD has been adapted in this research for use with capillary columns and

on-column injection. Adaptation of the HECD for capillary columns is presented in this section.

Experimental

The chromatographic instrumentation presented in Section III was modified for use with capillary GC columns. A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was interfaced to a J&W scientific fused silica, 30 m x 0.32 mm ID, capillary column with a 0.25 μm thick DB-5 bonded phase. Details of the capillary column interface to the HECD are presented below.

Airco grade 4.5 hydrogen with a hydrocarbon trap provided HECD reactor gas at 20 mL/min, carrier gas at 1 mL/min, and make-up gas at 40 mL/min. The HECD conductivity solvent, n-propanol, was pumped at 2 mL/min. The HECD base temperature was 300 ^{o}C and the nickel catalyst reactor temperature was 950 ^{o}C as recommended in Section IV. A Hewlett-Parkard Model 3390A integrator was used to determine the GC peak areas and retention times. The smallest available digital time constant for the integrator, 0.01 min., was used while monitoring eluates from the high resolution capillary column.

An SGE, OCI-3, on-column injector and syringe were used to deliver sample injection volumes less than 1 μL to the capillary column. The on-column injector was mounted on the Tracor 560 GC between the two already existing conventional injector parts. The injector heater blocks were not powered during experiments which utilized the on-column injector in order to minimize temperatures

in the injector region. Additional lowering of the on-column injector temperature was achieved by passing compressed air through internal cooling passages located in the on-column injector near regions adjacent to the GC oven. Carrier gas was delivered to the on-column injector through a precision flow control valve and pressure regulator. The pressure regulator maintained constant column head pressure.

Sample delivery began by opening a pneumatically controlled valve on the on-column injector and passing a specially designed syringe needle into the injector. The syringe needle is equipped with a special small-diameter fused silica tip which passes approximately 1 in. into the capillary column. After inserting the syringe needle, the pneumatic valve is closed, forming a seal around the syringe needle. The sample is injected slowly from the syringe onto the inside walls of the column after carrier gas flow has been reestablished through the column. Following sample delivery, the syringe is removed from the injector while maintaining a tight seal around the needle. The pneumatically controlled valve which maintains carrier gas flow through the column during the injection process, also allows hot on-column injection techniques to be used when needed.

HECD Time Constant Estimates

Detector design is important in capillary GC systems so that the high resolution achieved by the capillary column is not diminished significantly in the detector. Detector flow paths

should therefore be designed to minimize turbulent flow, and detector void volumes should be small to reduce detector response time constants. The detector volume, V_d, required to maintain column peak widths within $\theta \cdot 100\%$ at the detector can be expressed in terms of detector volumetric flow rate, F_d, analyte retention time, t_R, and total column plate number, P, [5]

$$V_d = \frac{\theta \cdot t_R \cdot F_d}{(P)^{1/2}} \qquad (21)$$

For example, equation 21 can be used to predict the required detector volume which will provide a detector contribution to peak widths below 1%, $\theta = 0.01$, for a retention time of 9 min. The particular 30 m X 0.315 mm capillary column used in these experiments has an effective total plate number of 74,500 at t_R = 9 min., according to manufacturer's data. Thus, a detector volume less than 0.33 µL is required to maintain column resolution in the detector within 1% if the detector volumetric flow rate was equivalent to the column flow rate of 1 mL/min. However, make-up gas may be added to column effluent prior to detection in order to increase detector volumetric flow for larger detectors. Accordingly, a detector volume of 20 µL can be tolerated in the above example if detector flow is increased to 60 mL/min via make-up gas introduction.

The effective HECD detector volume is difficult to calculate because it must include the two-phase nature of the flowing system. Column effluent, make-up gas and reaction gas all flow through the reactor assembly and transfer line and then into the

differential conductivity cell. Total gas flow rates are typically about 60 mL/min for the capillary-HECD system as described below. However, simple measured species are then distributed between reactor effluent gas and the conductivity solvent via gas-liquid extraction. The conductivity solvent, however, is only flowing at less than 2 mL/min for the capillary-HECD through the gas-liquid contactor. The HCl indicator species, dissolved in conductivity solvent, then flow through the lower conductivity cell where it is measured while the solvent is flowing at approximately 2 mL/min. Furthermore, the conductivity solvent does not fill the entire cell volume but only adheres to stainless steel walls, as pictorially presented in figure 27.

To complicate matters additionally, complete HECD component dimensions are not available in the published literature. However, Wenske at Tracor Instruments claimed the total HECD gas volume, V_G, to be about 100 μL and total analyte liquid volume, V_L, to be 3.7 μL [182]. The HECD contributions to measured peak widths due to the total gas volume and total liquid volume, θ_G and θ_L respectively, can be calculated from equation 21 based upon these data. θ_G then is 0.05, or 5%, for t_R = 9 min., at 60 mL/min total gas flow rate. Correspondingly, θ_L is 0.06 or 6% for the same retention time and 2 mL/min total solvent flow rate. Therefore measured peak widths for capillary column eluates should not broaden by more than 6% in the HECD detector at a total gas flow rate of 60 mL/min and solvent flow rate of 2 mL/min.

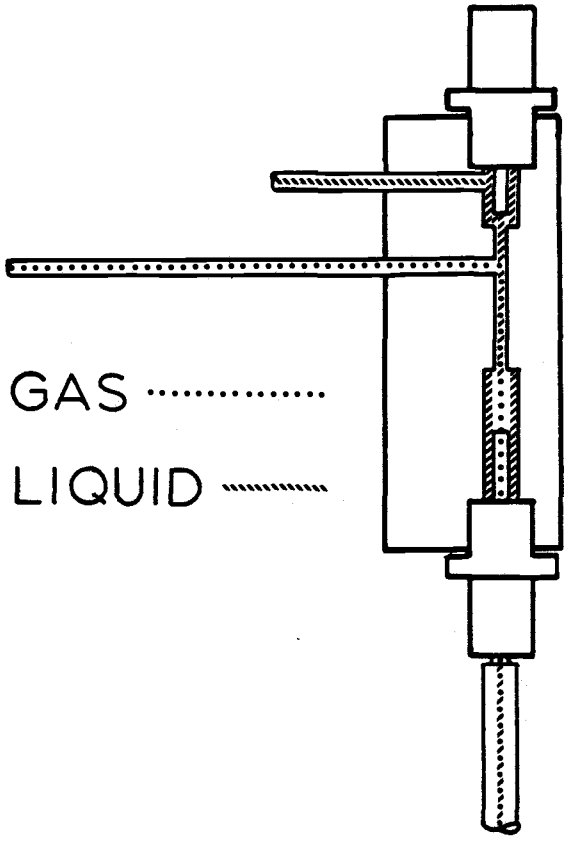

Figure 27. Gas and liquid flow regions of HECD.

Implementation of Capillary Columns with the HECD

Helium carrier gas with hydrogen reaction gas are typically used for the HECD and packed column systems. However, hydrogen carrier gas was used with capillary columns since hydrogen provides higher resolution than helium and also eliminates the requirement for two cylinders of purified gases [5]. Thus, hydrogen was used for carrier gas, reaction gas and make-up gas. Column connections inside the oven were always checked carefully for hydrogen leaks as a safety procedure.

The HECD is designed to accept the end of a 1/4 in OD packed GC column at the column-HECD interface in the reactor assembly (figure 2). To adapt the assembly for capillary systems, a 1/4 in OD x 1 mm ID x 4 in length glass insert was placed into the HECD column interface and anchored with a 1/4 in. graphite ferrule. A 1/4 in OD to 1/16 in OD stainless steel Swagelok reduction union, modified for make-up gas introduction, was attached to the other end of the glass insert (figure 28). The capillary column was passed through the reduction union into the center of the glass insert and located such that the termination of the capillary column was about 1 mm from the narrow entrance into the nickel catalyst reaction tube (figure 28). The capillary column was anchored by a 0.8 mm to 1/16 in OD graphite ferrule at the reduction union.

Hydrogen carrier gas flow was set to 1 mL/min with the precision flow control valve provided with the on-column injector after column head pressure was set at 30 psi. Hydrogen make-up gas, set at a flow rate of about 40 mL/min, was introduced through the

modified Swagelok reduction union. The make-up gas passed through the volume between the inner wall of the glass insert and the capillary column, sweeping eluents into the high temperature reactor. Hydrogen is also introduced through the reaction gas inlet at about 20 mL/min. The resulting total gas flow of 60 mL/min for the capillary HECD system approximates the optimal gas flow through a packed column HECD system of 70 mL/min (Table 8). The venting system operates effectively for the capillary HECD to divert most column effluent away from the detector during solvent peak elution, while maintaining positive flow through the HECD reactor and conductance cell. The capillary HECD system utilizes gas flows which are similar to conditions for which the HECD was designed and consistent with optimum HECD flow conditions presented in Section V.

HECD time constant estimates predict that conductivity solvent flows through the differential conductance cell of 2 mL/min result in measured peak width broadening of 6% in the detector for capillary systems. Solvent flow experiments with packed columns (figure 21) indicated that a flow rate of 0.5 mL/min was optimum, and indicated that the HECD response factor decreases dramatically when solvent flow increases. However, a conductivity solvent flow rate of 0.5 mL/min would yield a peak width increase of 22% in the HECD for capillary columns. Experimentally, the conductivity solvent flow rate of 2 mL/min provides sufficient HECD response times for capillary separations. Figures 29-34 in Section VIII, illustrate PCB separations obtained with the capillary-HECD system. Additional experiments conducted with flow rates in excess of 2 mL/min did

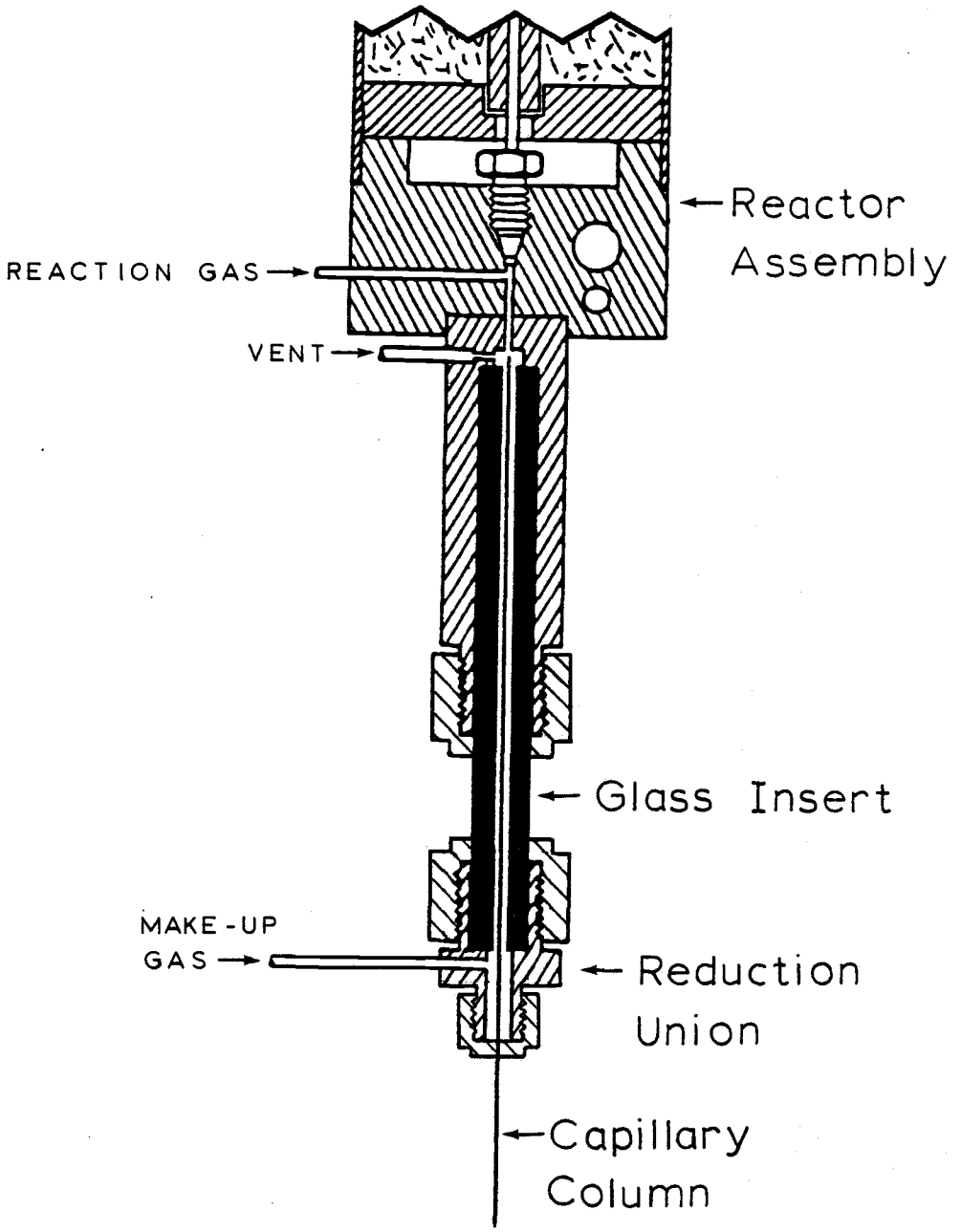

Figure 28. Capillary column interface to the HECD reactor assembly.

not result in improved peak widths, but further reduced the HECD response factor. Thus, an HECD solvent flow rate of 2 mL/min is used with capillary column systems for PCB measurements presented in Section VIII.

The adapted HECD permits adequate response times for detection of high resolution separations with capillary columns. However, a HECD detector system designed with smaller detector volumes could further enhance resolution of the HECD system. Such a system is reportedly now be available from the O-I Corporation: they presented a new electrolytic conductivity detector, designed for capillary systems, at the March, 1985 Pittsburgh Conference. However, this new equipment was not evaluated in this thesis research.

VIII. DETERMINATIONS OF POLYCHLORINATED BIPHENYL ISOMERS BY RESPONSE FACTOR CALIBRATION

Summary

The measurement of polychlorinated biphenyl (PCB) isomers by Response Factor Calibration (RFC) was evaluated with gas chromatography and the Hall electrolytic conductivity detector (GC-HECD). RFC determinations for ten PCB isomers, contained in a test material reference solution are compared to the supplier's stated concentrations. Precision is best for RFC measurements of isomer peaks which elute near the response standard. Weight percent chlorine is also determined for five Aroclor mixtures by RFC and compare well with the manufacturer's individual stated weight percent chlorine. PCB isomers are determined and quantitatively compared in the same Aroclor mixtures with RFC procedures. Supplemental GC-MS data provides stoichiometric information for PCB determinations in mass units. However, complete identification of PCB isomers is not required, and reference materials which contain the specific PCB isomers of interest are not required.

Introduction

Measurements of PCBs at trace concentrations in complex samples provide several challenges for analytical chemists. Although, PCBs generally exhibit thermal stability, low volatility, and low LODs in typical GC analyses, the 209 possible PCB congeners may not be

completely resolved with capillary GC columns. Mullin, et al. synthesized and prepared analyte standards for all 209 PCB isomers, and characterized chromatographic properties for these eluates [28]. The best capillary GC separations could resolve 187 PCB isomers, but 11 PCB pairs were not resolved.

Determinations of individual PCB isomers via established quantitative GC methods require reference solutions which contain the specified PCB isomers of interest at known concentrations. Thus, complex PCB determinations require reference solutions which contain an array of PCBs at well established concentrations.

Aroclor mixtures are routinely employed as test materials for PCB determinations, even through the concentrations for many individual PCB isomers are not well established or are unknown. Aroclor mixtures are obtained by chlorinating biphenyl to achieve a particular specified total weight percent chlorine [30, 31]. The weight percent chlorine and average number of chlorines per molecule are listed in Table 9 for eight Aroclor mixtures. Researchers have identified many PCB isomers contained in these Arochlor mixtures and measured their relative retention times [29, 30, 31, 32]. However ambiguities persist for complete PCB isomer identifications in Aroclor mixtures.

Pattern recognition techniques have been used to compare eluted PCBs with Aroclor mixtures [33, 34, 35, 36]. These techniques employ the Aroclor mixtures as test materials and determine all PCB analytes together in units of mass of a particular Aroclor mixture. This requires valid identification of the sample PCB content as a specified Aroclor mixture. However, if a gas

Table 9. Weight percent chlorine and the average number of chlorines per PCB molecule for eight Aroclor mixtures.

Aroclor	% Cl	Average number Cl/molecule
1221	21	1.1
1232	32	2.0
1242	42	3.1
1248	48	3.9
1254	54	4.9
1260	60	6.3
1262	62	6.8
1268	68	8.7

chromatogram cannot be validly matched to an Aroclor mixture, then quantitation in units of specified Aroclor mass is not possible [28].

Webb characterized Aroclor mixtures using a Coulson detector without employing PCB reference materials [19]. For that work, the Coulson detector response was assumed to be linear with organochlorine concentration. Similarly, Nulton, et al., utilized the HECD detector for total organochlorine determinations of environmental samples [128].

Chlorinated hydrocarbons have been successfully determined in the absence of identical analyte reference materials by response factor calibration (RFC) as discussed in Section III [20, 21]. Criteria were reported in Sections IV - VI for employing the Hall electrolytic conductivity detector for RFC measurements [20, 21]. PCB isomer determinations by RFC with GC-HECD in the absence of reference materials which contain each isomer, or complete isomer identification are reported in this section. The measurements employ an HECD which has been adapted for use with capillary GC columns as described in Section VII.

Experimental

Reagents

A test material, DCMA PCB mixture, containing 10 PCB isomers in n-hexane was purchased from Supelco, Inc. The 10 PCB isomers were 2-chlorobiphenyl, 3,3-dichlorobiphenyl, 2,4,5-trichlorobiphenyl,

2,2',4,4'-tetrachlorobiphenyl, 2,3',4,5',6-pentachlorobiphenyl, 2,2',3,3',6,6'-hexachlorobiphenyl, 2,2',3,4,5,5',6-heptachlorobiphenyl, 2,2',3,3',4,4',5,5'-octachlorobiphenyl, 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl, and decachlorobiphenyl. The PCB test material was prepared by gravimetric techniques at 0.5% uncertainties. PCB mixtures were provided by the U.S. Environmental Protection Agency: Aroclors 1221, 1232, 1242, 1248, 1254 and 1260.

α,α,α-trichlorotoluene (TCT, 99+% pure) was purchased from Aldrich Chemical Company, and 2-chloronaphthalene (2CN, 99.8% pure) was provided by the U.S. Environmental Protection Agency. Resianalyzed grade n-hexane and n-propanol solvents were purchased from J.T. Baker Chemical Co.

Procedures

2-chloronaphthalene and α,α,α-trichlorotoluene were used as response standards due to high purity, stability and appropriate GC retention time. The 2CN response standard solution was 0.61 μmol Cl/mL and the TCT response standard solution was 0.84 μmol Cl/mL.

Aroclor mixtures were diluted by 10 to yield 500 μg/mL, total Aroclor concentration, and the response standards were included at 0.061 μmol Cl/mL and 0.084 μmol Cl/mL for 2CN and TCT, respectively. The Supelco PCB mixture was diluted by 2 to yield the PCB isomer concentrations listed in Table 10. 2CN and TCT response standards were included in the diluted PCB standard solution at 0.061 μmol Cl/mL and 0.084 μmol Cl/mL, respectively. Acid washed, hexane rinsed glassware was used in all dilutions and

Table 10. Stated and measured concentrations for 10 PCB isomers contained in the Supelco test material. 90% confidence intervals are based on the t-statistic and measured standard deviation for n = 7 [153].

PCB Isomer	PCB Isomer Concentrations (μmol Cl/mL)				% Difference Between Stated & Meas. Conc.
	Stated Conc.	Measured Conc. by RFC	90% Confidence Interval	as % of stated conc.	
monochlorobiphenyl	0.53	0.53	0.014	2.6	4
dichlorobiphenyl	0.90	1.05	0.043	4.8	17
trichlorobiphenyl	0.12	0.14	0.008	6.7	17
tetrachlorobiphenyl	0.14	0.17	0.011	7.9	22
pentachlorobiphenyl	0.15	0.19	0.014	9.3	26
hexachlorobiphenyl	0.17	0.23	0.019	11	35
heptachlorobiphenyl	0.089	0.097	0.009	10	10
octachlorobiphenyl	0.093	0.10	0.010	11	13
nonachlorobiphenyl	0.097	0.11	0.010	9.9	12
decachlorobiphenyl	0.10	0.10	0.009	8.6	0.2

storage. Class A volumetric glassware and n-hexane were used for all dilutions.

Chromatographic Instrumentation

A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was interfaced to a J&W scientific, 30 m x 0.32 mm ID fused silica, capillary column with a 0.25 μm DB-5 bonded phase.

The HECD reactor assembly was adapted for capillary systems. A 1/4 in OD x 1 mm ID x 4 in length glass insert was placed into the HECD column interface and anchored with a 1/4 in graphite ferrule. A 1/4 in OD to 1/16 in OD stainless steel Swagelok reduction union, modified for make-up gas introduction, was attached to the other end of the glass insert. The capillary column was passed through the reducing union into the center of the glass insert and located such that the termination of the capillary column was about 1 mm from the narrow entrance into the nickel catalyst reaction tube. The capillary column was anchored by a 0.8 mm to 1/16 in OD graphite ferrule at the reduction union.

An SGE OCI-3 on-column injector and syringe were used to deliver sample injection volumes of 0.4 μL to the capillary column. Hydrogen carrier gas flow was set to 1 mL/min with the precision flow control valve provided with the on-column injector, and column head pressure was set at 30 psi. Hydrogen make-up gas, set at a flow rate of about 40 mL/min, was introduced through the modified Swagelok reducing union. Hydrogen was also introduced

through the reaction gas inlet at 20 mL/min. The resulting total hydrogen gas flow for the capillary HECD system was 60 mL/min. The HECD conductivity solvent, n-propanol, was pumped at 2 mL/min which provides an adequate detector time constant for capillary peak widths as discussed in Section VII. The HECD base temperature was 300 ^{o}C and the nickel catalyst reactor temperature was 990 ^{o}C.

Aroclors and PCBs were separated by a GC temperature program from 130 ^{o}C to 275 ^{o}C, increased at 2 ^{o}C/min, after a 3 min isothermal period at 130 ^{o}C. The response standards were completely resolved from PCB isomers present in the Aroclor mixtures. A Hewlett-Packard Model 3390A integrator was used to measure the GC peak areas and retention times.

GC-MS Instrumentation

Stoichiometric data such as the number of chlorines per molecule and molecular weight for individual PCB isomers of interest were obtained by GC-MS. A Finnigan 4023 GC-MS was used to obtain mass spectra. The system's 4500 ion source was utilized in the electron impact mode at 70 eV and 190 ^{o}C. The mass spectrometer scanned between 50-600 m/z at 1 second intervals.

The same capillary column and temperature program used with the adapted GC-HECD were employed for PCB separations with the GC-MS system. Sample injection volumes of 3 μL were introduced during a 1.5 min. splitless injection period, and the helium carrier gas flow rate was 1.8 mL/min. Eluate peaks observed in the reconstructed ion chromatograms and corresponding mass spectra were

related to the capillary-HECD eluate peaks via relative retention times.

Results and Discussion

The ten PCB isomers contained in the Supelco test material were separated by GC-HECD (figure 29). Analyte peak areas and the 2CN response standard peak area were obtained from seven replicate chromatograms. RFC calculations yielded the isomer concentrations in μmoles Cl/mL as listed in Table 10 [20]. The 90% confidence interval sizes, based on the t-statistic and measured standard deviations for seven replications, are less than 10% of the stated isomer concentrations except for the hexachloro and octachloro PCB isomers [153]. The confidence interval sizes, as a percent of the stated isomer concentration, reveal good precision. However, the confidence intervals contain the stated isomer concentrations for only the monochloro, heptachloro, octachloro and decachloro PCB isomers.

Evaluating RFC measurements for PCB isomers is difficult in the absence of reliable accuracy information for this PCB test material. RFC determinations by GC-HECD require quantitative analyte reduction in the high temperature HECD reactor [21]. A reactor temperature of 990 ^{o}C, utilized during these experiments has been shown to provide quantitative analyte reduction for many chlorinated hydrocarbons as described in Section IV [21]. However, if differences between measured and stated concentrations for the Supelco test material were due to incomplete analyte reduction,

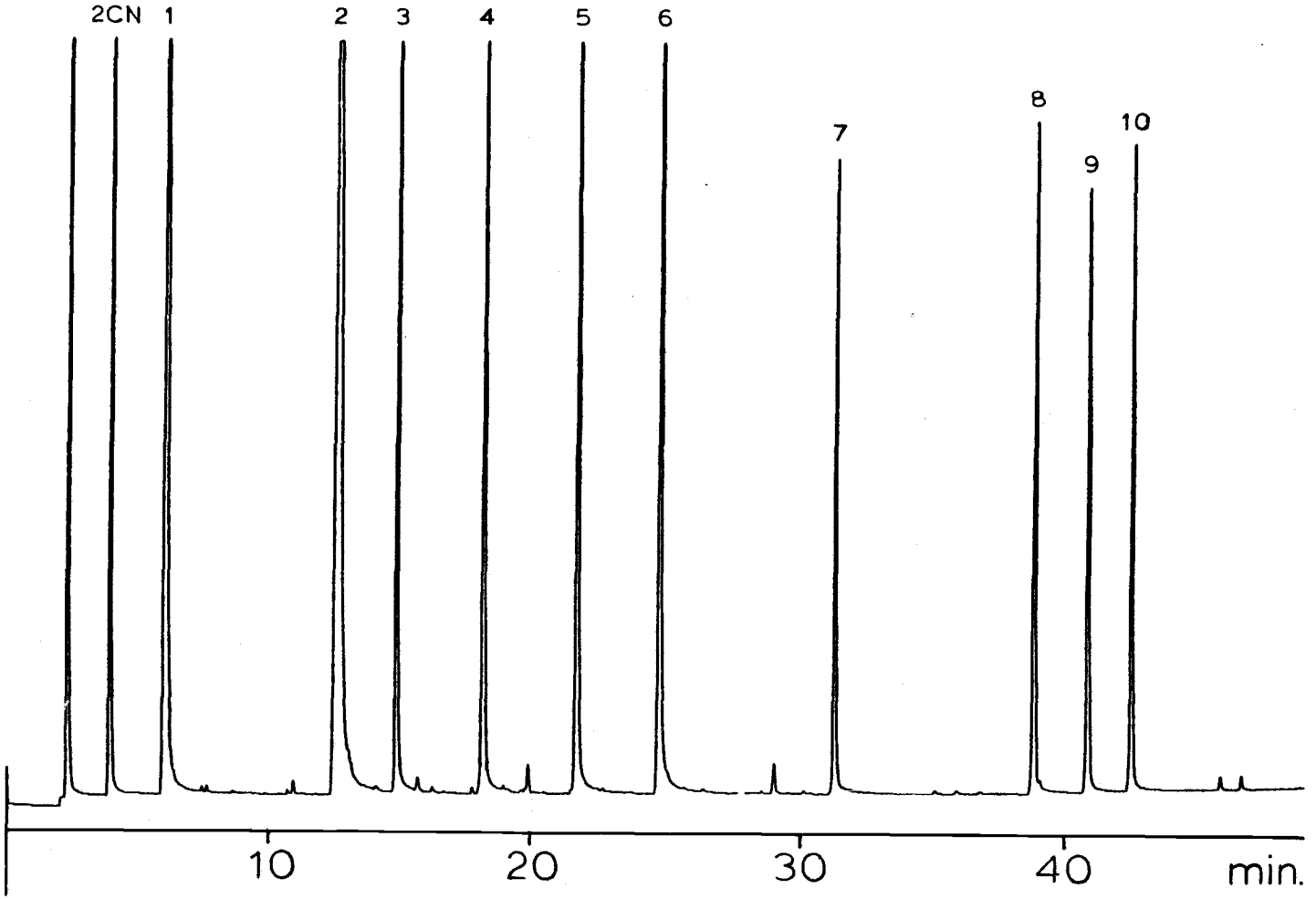

Figure 29. Capillary HECD chromatogram of ten PCB isomers contained in the Supelco test material. 2CN is the response standard and numbers 1 - 10 indicate the number of chlorines per PCB isomer.

then the measured concentrations should be less, not greater, than stated concentrations (Table 10). Thus, incomplete analyte reduction does not account for differences between measured vs. stated analyte concentrations for the Supelco test material. Therefore the supplier's stated concentrations for several PCB isomers contained in the test material are suspect. Unfortunately, alternative certified PCB test materials are unavailable which precludes appropriate evaluation of the accuracy of these RFC experiments.

Determination of Weight Percent Chlorine for Aroclor Mixtures

The total weight percent chlorine was measured by RFC for five Aroclor mixtures, 1221, 1232, 1242, 1254 and 1260. Figures 30-34 show representative GC-HECD chromatograms for each of the Aroclor mixtures, respectively.

The emergence of more highly chlorinated PCB isomers as the weight percent chlorine increases, Aroclors 1221 to 1260, can be observed in Figures 30-34. Generally, analyte retention times progressively increase with increasing numbers of chlorine per PCB as observed for the Supelco test material (figure 29). Mass spectra obtained for Aroclor mixtures and the Supelco test material corroborate the increasing retention time trend. Figures 30-34 reveal that the Aroclor's major isomer peaks elute after longer retention times as Aroclor weight percent chlorine increases. Thus, Aroclor 1221 and 1232 contain PCB isomers with fewer chlorines while isomers contained in Aroclors 1242, 1254 and 1260

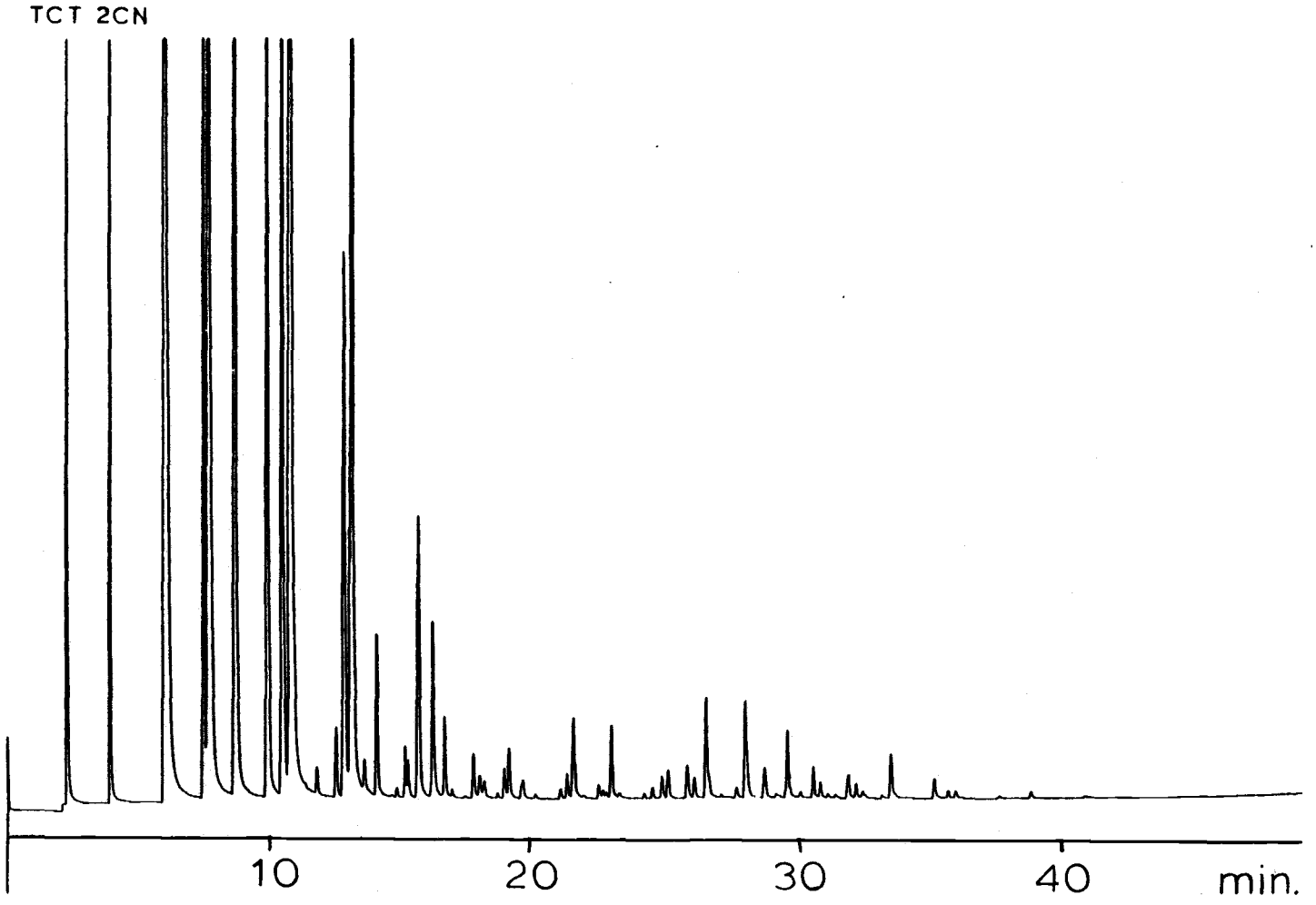

Figure 30. Capillary HECD chromatogram of Aroclor 1221. 2CN and TCT are included as response standards.

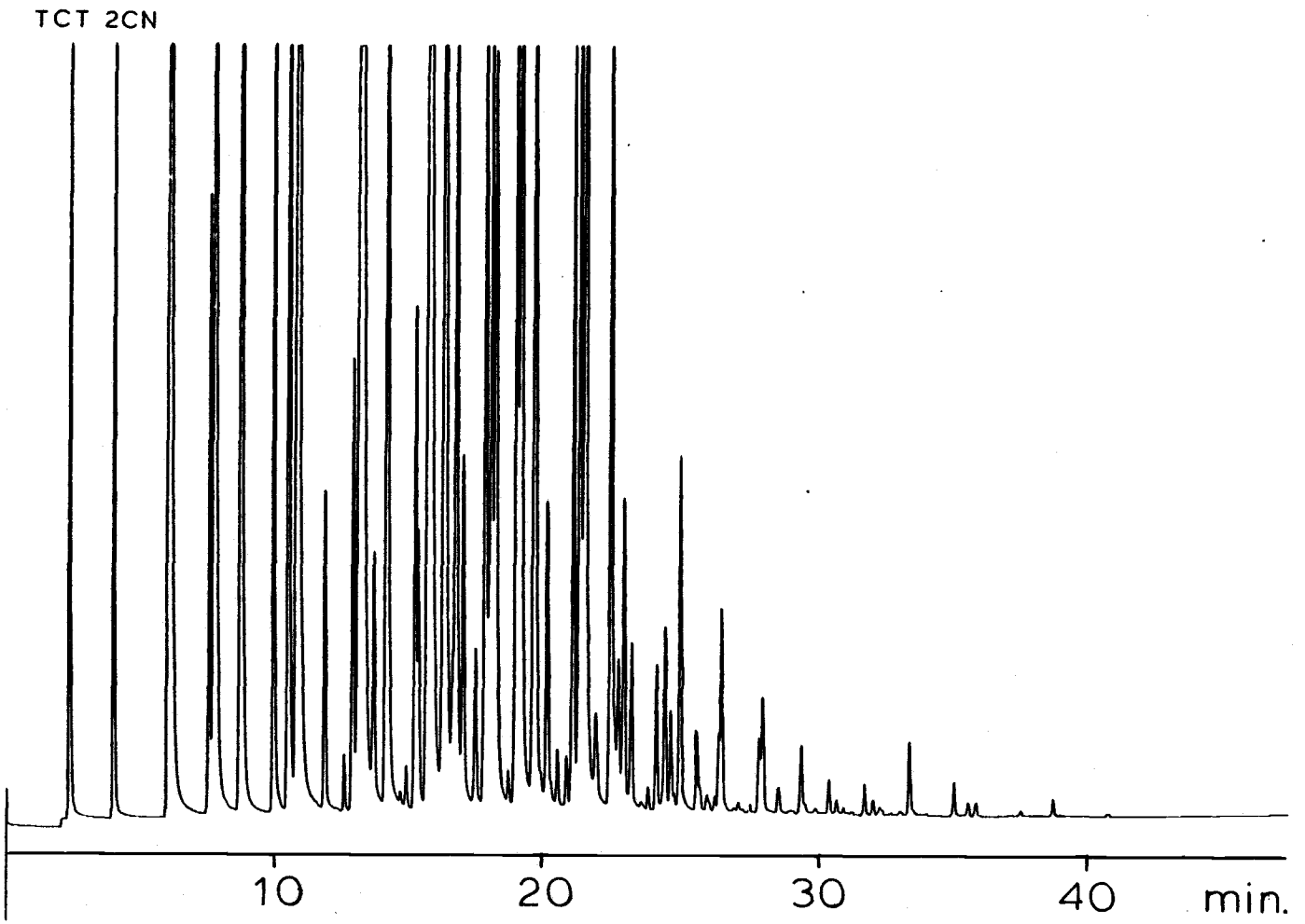

Figure 31. Capillary HECD chromatogram of Aroclor 1232. 2CN and TCT are included as response standards.

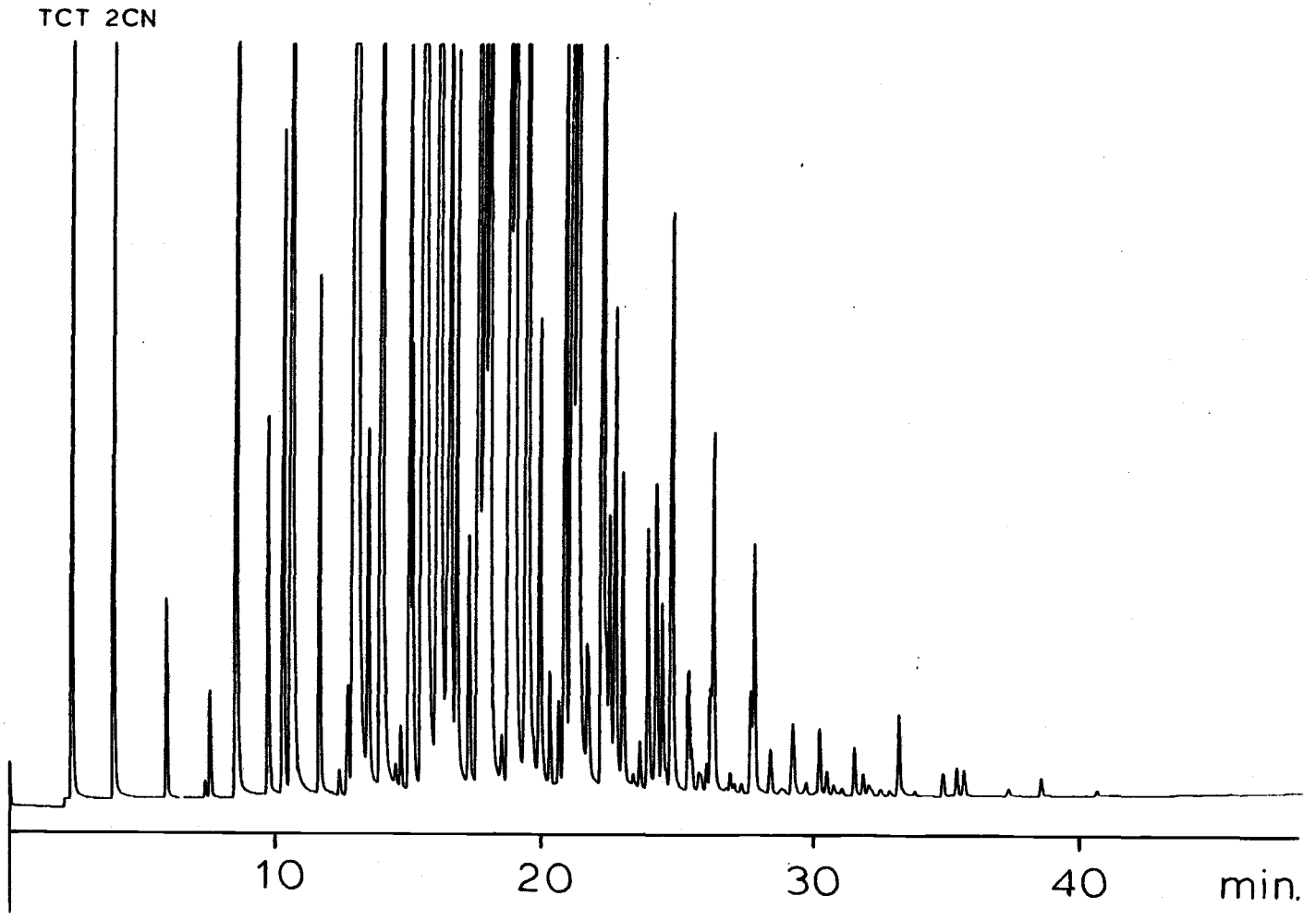

Figure 32. Capillary HECD chromatogram of Aroclor 1242. 2CN and TCT are included as response standards.

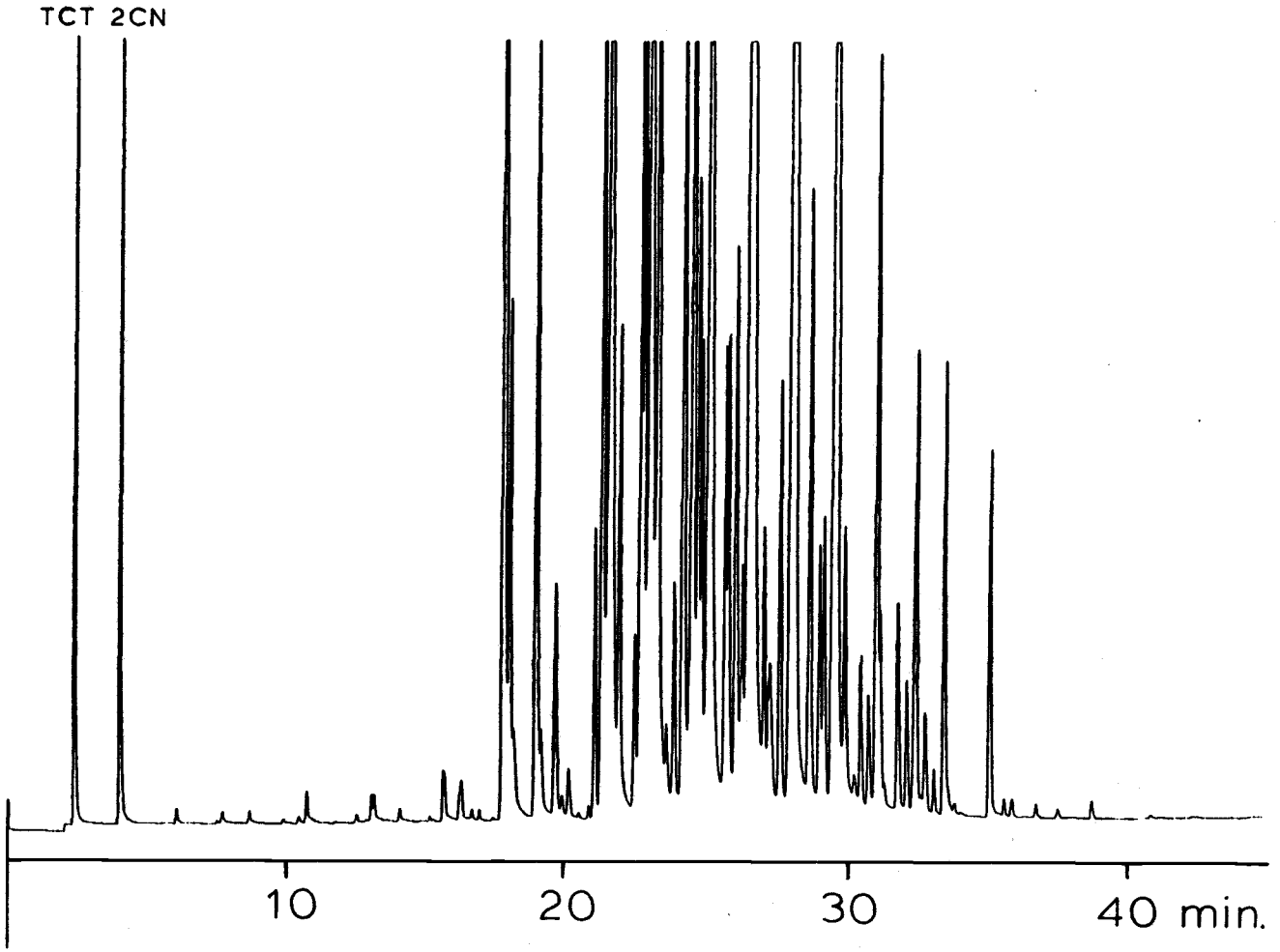

Figure 33. Capillary HECD chromatogram of Aroclor 1254. 2CN and TCT are included as response standards.

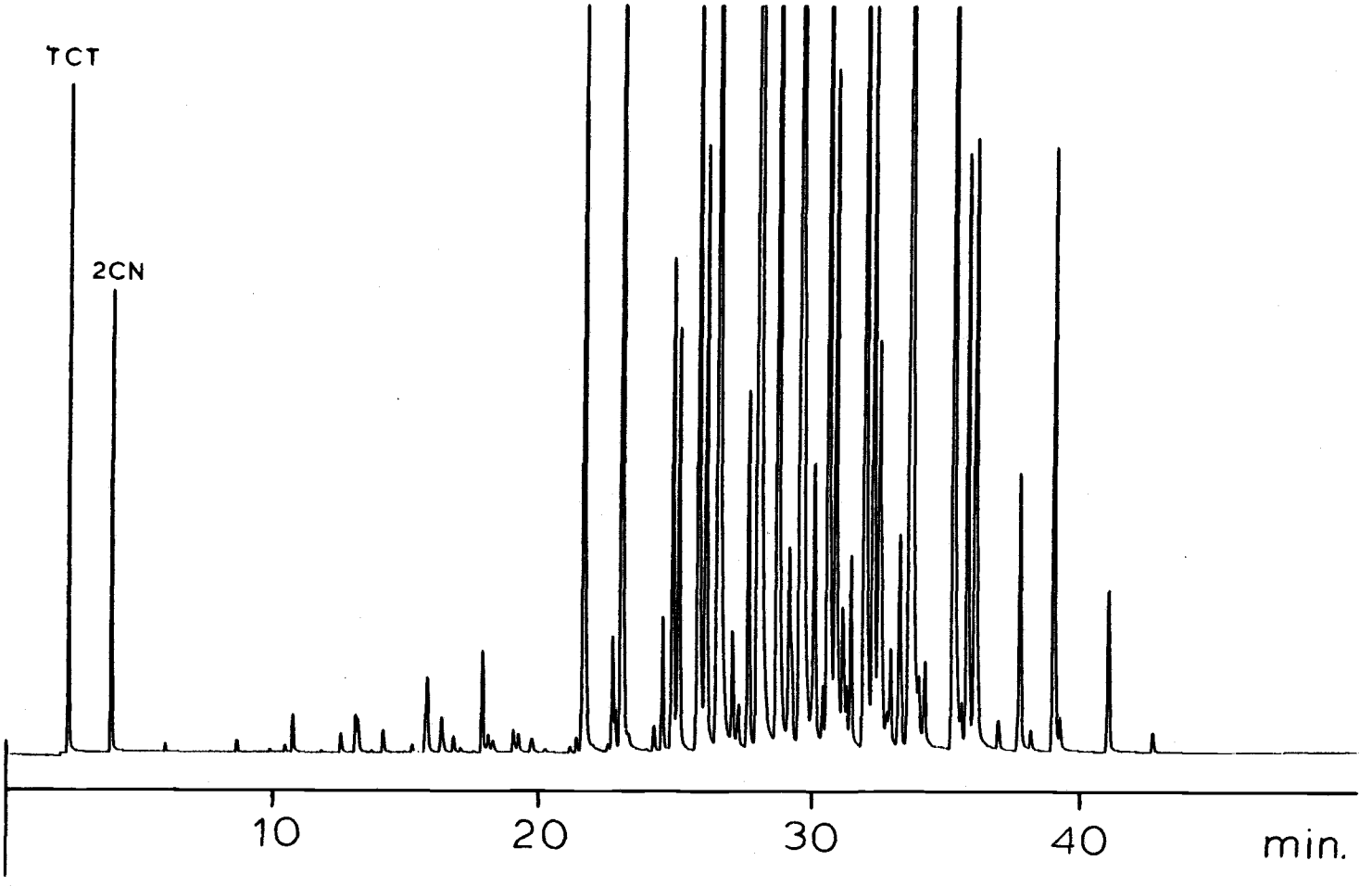

Figure 34. Capillary HECD chromatogram of Aroclor 1260. 2CN and TCT are included as response standards.

are more highly chlorinated. Table 9 shows a similar increasing trend for the average number of chlorines per molecule as weight percent chlorine increases in several Aroclor mixtures.

Peak areas, excluding the response standards and HECD solvent venting peaks, were summed and compared to 2CN and TCT response standard peak areas. RFC measurements yielded the total weight percent chlorine values listed in Table 11, using 2 or 3 data points.

The measured weight percent chlorine and stated weight percent chlorine agree within 7%, except for Aroclor mixture 1254: this is good agreement. However, the RFC measurements are larger than stated values for Aroclors 1221 and 1232, but smaller for Aroclors 1242, 1254 and 1260. The trend from positive differences between RFC measured weight percent chlorine and stated weight percent chlorine values for less chlorinated Aroclors to negative differences for more highly chlorinated Aroclor mixtures, introduces some suspicion for RFC measurements of highly chlorinated PCB isomers.

If increasing the number of chlorines per PCB isomer enhances compound stability, then highly chlorinated isomers, more prevalent in Aroclors 1242, 1254 and 1260, could be more difficult to reduce in the high temperature HECD reactor. Thus, incomplete analyte reduction in the HECD reactor may exist for very highly chlorinated PCBs, and a small percentage of these eluates may not produce the simple measured species, HCl.

Table 11. Stated and RFC measured weight percent chlorine content for five Aroclor mixtures.

Aroclor	Weight Percent Chlorine		Percent Difference Between Stated and Measured Chlorine Weight Percent
	Stated Percent Chlorine	Percent Chlorine by RFC	
1221	21	22	2
1232	32	34	7
1242	42	40	5
1254	54	47	14
1260	60	57	5

Determination of Individual PCB Isomers in Aroclors

Particular PCB isomers were determined in the five Aroclor mixtures by RFC. Relative retention times were used to compare isomer peaks from different elutions. PCB isomer concentrations were determined in μmol of Cl/mL from the response ratio, relative to 2CN, and the 2CN concentration in solution [20] (Table 12). Each PCB isomer determination included 2 or 3 data points.

Supplemental GC-MS data were used to obtain the number of chlorine atoms per molecule and molecular weights for PCB isomers of interest. PCB isomer concentrations were then determined in μg of analyte/mL, using GC-MS stoichiometric information and isomer concentrations determined in μmol Cl/mL (Table 12) [20]. Stoichiometric information was not found for the PCB isomer observed at a relative retention time of 9.84; this isomer was present below the limit of detection for the GC-MS system.

Selected PCB isomers were determined in the absence of identical PCB isomer reference materials and complete isomer identification was not required for determinations. Stoichiometric information, obtained by GC-MS, did not include complete identification of the particular PCB isomer.

Unfortunately, accuracy information could not be included for these RFC determinations of PCB isomers, since a reliable reference material for individual PCB isomers is not available. However, the absence of reference materials which contain well characterized PCB isomers restricts the usage of established chromatographic methods for determinations of individual PCB isomers. Thus, RFC provides

Table 12. RFC determination and comparison of five selected PCB isomers contained within five Aroclor mixtures.

PCB Isomer	Relative Retention Time	Number Chlorines Per PCB	Molecular Weight	PCB Isomer Conc. (μg/mL) in Aroclors, 500 μg total PCBs Isomer Conc. (μmol Cl/mL) in parentheses				
				1221	1232	1242	1254	1260
1	1.52	1	188.66	140 (0.74)	77 (0.41)	2.5 (0.013)	0.23 (0.0012)	0.13 (0.0007)
2	3.57	3	257.55	1.6 (0.0187)	14 (0.17)	21 (0.25)	---- ----	0.25 (0.0029)
3	3.99	3	257.55	3.6 (0.042)	40 (0.47)	58 (0.67)	0.37 (0.0043)	0.86 (0.010)
4	7.17	6	360.88	0.96 (0.016)	0.78 (0.013)	0.27 (0.0045)	5.0 (0.083)	57 (0.95)
5	9.84	----	----	---- ----	---- (0.0014)	---- (0.0017)	---- (0.0019)	---- (0.16)

improvements in PCB isomer determinations over other established chromatographic methods, which require PCB isomer reference materials and complete isomer identification.

IX. CONCLUSIONS

Analyte reference materials are normally required by established chromatographic methods for analyte determinations. Thus the absence of appropriate analyte reference materials for analytes of interest presents severe limitations when quantitative measurements are needed. Analytical chemists, recognizing this problem, typically devote extensive effort toward analyte identifications and subsequent preparation of reliable reference materials prior to analyte determinations. However, such extensive efforts are sometimes neither economic nor feasible. For such cases chromatographic methods may be developed which permit quantitative measurements in the absence of reference materials which contain the analytes of interest and without complete analyte identification. Response factor calibration (RFC), developed herein, is such a procedure.

RFC is used with analytical systems which provide quantitative production of the same simple measurable species, both from analytes of interest and the response standard. The response standard is employed to measure the instrumental response factor for the simple species during each elution. Analytes of interest can then be determined in simple species equivalents, using the response factor obtained via the response standard. Additional stoichiometric information, such as the simple species equivalents per mole of analyte or molecular weight, allow analyte determinations in mass units. However, neither identical analyte

reference materials nor complete identification are required prior to determination by RFC.

RFC procedures were developed and successfully applied in this research to determinations of chlorinated hydrocarbons with GC-HECD. Chlorinated analytes are catalytically reduced to HCl, the simple species, and HCl is subsequently measured by conductometry. HCl is an indicator substance for organochlorine. Calibration curves were developed to relate analyte organochlorine equivalents to the HECD response. The relationship between analyte peak areas, relative to response standard peak areas, and analyte organochlorine equivalents is linear over several orders of magnitude for the chlorinated hydrocarbons evaluated. In addition, criteria for RFC determinations with GC-HECD were developed: reactor temperature selection, HECD flow rates, constant carrier gas flow control, and implementation of capillary columns with the HECD. As an example, RFC was applied to determinations of unidentified hexachlorocyclopentadiene photolysis products. Analyte organochlorine equivalents were successfully measured during the photolysis experiment to monitor quantitatively analyte degradation after various exposure time intervals.

HCl, the simple species for chlorinated hydrocarbons, is produced by high temperature catalytic reduction in the HECD reactor and measured by conductometry. Reduction efficiencies of organochlorine to HCl can be measured for analytes to provide HECD reactor temperature selection criteria. The HECD reactor products weremonitored by mass spectrometry, using a GC-HECD-reactor-MS system. Quantitative reduction of organochlorine to HCl are

observed for chlorinated hydrocarbons when reactor temperatures exceeded 950 ^{o}C.

Flow conditions for the HECD were evaluated by a three factor, three level, central composite factorial experiment. A second order, ten parameter polynomial model was used to describe a response surface, and estimate the relationship between the three flow factors and the HECD response. Trends revealed by the response surface can be used to select optimum flow conditions for the HECD with packed or capillary GC columns. Conductivity solvent flow exhibits the largest affect of the three factors on HECD response. Additionally, both reaction gas and carrier gas flows significantly affect the HECD response. A microprocessor controlled system can be used to maintain constant carrier gas flow in packed GC columns during temperature programmed analyses with the HECD.

RFC can successfully be used for the determination of chlorinated hydrocarbons by GC-HECD with both packed or capillary GC columns. The adapted capillary-HECD system developed herein provides high resolution analyte separation and measurement, and column peak widths are only broadened by approximately 6% in the adapted HECD. The resolution of the capillary-HECD system is sufficient for determinations of individual PCB isomers by RFC.

PCB standards, containing one to ten chlorines per biphenyl, were measured by RFC, and compared to the PCB standard concentrations as stated by the supplier. Total organochlorine equivalents for Aroclor mixtures were also measured by RFC and

calculated weight percent chlorine values compared well with expected chlorine contents for several Aroclors.

RFC procedures can be useful for analyte determinations in the absence of reference materials which contain the analytes of interest and complete analyte identification. Typically, quantitative measurements are difficult or impossible under such conditions when established methodologies are employed. Future studies and experiments are suggested in Section X for the further development of RFC techniques.

X. RECOMMENDATIONS FOR FUTURE STUDIES

A. Response Factor Calibration with GC-HECD.

1. Evaluate other chlorinated hydrocarbons and PCB standards by RFC with GC-HECD to find analytes which deviate from the developed calibration curve. Obtain, if available, a certified reference material which contains several PCB isomers.
2. Perform detailed temperature studies on organochlorine reduction to HCl for analytes which deviate from the calibration curve.
3. Evaluate chlorinated analytes which contain other elements in addition to chlorine, carbon and hydrogen, i.e., fluorine, bromine, iodine, oxygen, sulfur, nitrogen and phosphorus. Indicate elements and functional groups which act as interferents in RFC with GC-HECD.
4. Develop methodology to identify potential interferents in analytes to be determined by RFC, and analytes which deviate from the calibration curve. One might use mass spectrometry and possibly NMR techniques to accomplish these identifications. Such identifications would only need to exclude the presence of interferents or particular analytes in order to validate results, not necessarily provide positive identification for the specific interferents or analyte of interest.

B. Response Factor Calibration with GC and the O-I Corporation electrolytic conductivity detector.

1. Evaluate this new electrolytic conductivity detector, designed specifically for capillary GC columns. Employ evaluation techniques similar to those used with GC-HECD.

C. Response Factor Calibration using other techniques.

1. Identify and evaluate analytical systems which may provide quantitative production of a measurable simple species, or several species, from analytes.

2. Investigate the microwave induced plasma system with gas chromatography for use with RFC. Produce simple measured species in a high temperature plasma which are subsequently measured.

3. Investigate expanded uses for the GC-HECD-reactor-MS system.

   a. Replace the packed column GC and diffusion pumped MS systems with a capillary GC and turbo-molecular pumped MS. For example, interface a HP 5880 GC to the HECD reactor and then to an HP mass selective detector system.

   b. Investigate techniques to improve efficiencies for the catalytic furnace.

   c. Investigate using the improved GC-reactor-MS system for RFC determinations. Utilize the reactor to produce simple ionizable species from analytes, which are measured by the MS system.

REFERENCES

1. J.P. Cali, Z. Anal. Chem. 297 (1979) 1.

2. ISD Guide. 6-1977 (E), Citation of Reference Materials in International Standards, International Organization for Standardization, Geneva, Switzerland, 1977.

3. R.W. Seward, Standard Reference Materials and Meaningful Measurements, Proc. of the 6th Materials Research Symposium, Institute for Materials Research, National Bureau of Standards, Gaithersburg, Maryland, 1973, pp. 121, 127.

4. K. Kafadar, K.R. Eberhardt, J. Research NBS, 88 (1983) 37.

5. M.L. Lee, F.J. Yang, K.D. Bartle, Open Tubular Column Gas Chromatography: Theory and Practice, John Wiley and Sons, New York, 1984, pp. 221-226.

6. L.R. Snyder, J.U. Kirkland, Introduction to Modern Liquid Chromatography, 2nd edition, John Wiley and Sons, New York, 1979, pp. 549-556.

7. H.Y. Tong, F.W. Karasek, Anal. Chem., 56 (1984) 2124.

8. H.Y. Tong, F.W. Karasek, Anal. Chem., 56 (1984) 2129.

9. L.Z. Pearcy, S.P. Rowland, C.H. Mack, E.E. Coll, J. Gas Chromatogr., 6 (1968) 173.

10. G. Perkins, Jr., R.E. Laramy, L.D. Lively, Anal. Chem., 35 (1963) 360.

11. R.W. Edwards, J. Chromatogr., 153 (1978) 1.

12. W.C. Askew, K.D. Maduskar, J. Chromatogr. Sci., 9 (1971) 702.

13. D.E. Elliott, J. Chromatogr. Sci., 15 (1977) 475.

14. W.L. Fitch, A.D. Sauter, Anal. Chem., 55 (1983) 832.

15. J.W. Otvos, D.P. Stevenson, J. Am. Chem. Soc., 78 (1956) 546.

16. F.W. Lampe, J.L. Franklin, F.H. Field, J. Am. Chem. Soc., 79 (1957) 6129.

17. A.G. Harrison, E.G. Jones, S.K. Gupta, G.P. Nagy, Can. J. Chem., 44 (1966) 1967.

18. G.F. Crable, N.D. Goggeshall, Anal. Chem., 30 (1958) 310.

19. R.G. Webb, A.C. McCall, J. Chromatogr. Sci., 11 (1973) 366.

20. T.L. Ramus, S.J. Hein, L.C. Thomas, J. Chromatogr., 314 (1984) 243.

21. T.L. Ramus, L.C. Thomas, J. Chromatogr., 328 (1985) 342.

22. R. Edwards, Chem. Industr., November 20, 1971, 1340.

23. S. Miller, Environ. Sci. Technol., 16 (1982) 98A.

24. N.A. Kirsken, Am. Lab., December 1981, 65.

25. T. Cairns, E.G. Siegmond, Anal Chem., 53 (1981) 1183A.

26. S. Miller, Environ. Sci. Technol., 17 (1983) 11A.

27. G. Weaver, Environ. Sci. Technol., 18 (1984) 22A.

28. M.P. Mullin, C.M. Pochini, S. McGrindle, M. Romkes, S.H. Safe, L.M. Safe, Environ. Sci. Technol., 18 (1984) 468.

29. D.L. Stalling, I.N. Huckins, J. Assoc. Official Anal. Chem., 54 (1971) 801.

30. D. Sissons, D. Welti, J. Chromatogr., 60 (1971) 15.

31. J. Armour, J. Chromatogr., 72, 1972) 275.

32. K. Ballschmitter, M. Zell, Z. Anal. Chem., 302 (1980) 20.

33. W.J. Dunn, D.L. Stalling, T.R. Schwartz, J.W. Hogan, J.D. Petty, E. Johansson, S. Wold, Anal. Chem., 56 (1984) 1308.

34. J.E. Picker, B.N. Colby, The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, 1983.

35. P.W. Albro, C.E. Parker, J. Chromatogr., 197 (1980) 155.

36. W. Blum, Applications Tip No. 35, Finnigan Instrumental Corp., 1971.

37. N.L. Gregory, J. Chem. Soc. (B), (1968), 295.

38. M. Godefroot, M. Stechele, P. Sandra, M. Verzela, J. High Resolut. Chromatogr. Chromatogr. Comm., 5 (1982) 75.

39. J.D. Millar, R.E. Thomas, H.J. Schattenberg, Anal. Chem., 53 (1981) 214.

40. T. Cairns, E.G. Siegmund, Anal. Chem., 53 (1981) 1599.

41. R.S. Collard, M.M. Irwin, Jr., Talanta, 30 (1983) 811.

42. R.J. Steichen, R.G. Tucker, E. Mechon, J. Chromatogr., 236 (1982) 113.

43. J.C. Duinker, M.T.J. Hillebrand, Environ. Sci. Technol., 17 (1983) 449.

44. J.W. Eichelberger, L.E. Harris, W.L. Budde, Anal. Chem., 46 (1974) 227.

45. K. Krupcik, P.A. Leclercq, A. Simoua, P. Suchanek, M. Collak, W. Hrivnak, J. Chromatogr., 119 (1976) 271.

46. H.M. McNair, E.J. Bonelli, Basic Gas Chromatography, 5th ed., Varian Aerograph, Walnut Creek, Calif., 1969, pp. 118-119.

47. C.H. Hartman, Anal. Chem., 43 (1972) 124A.

48. P. Slade, J. Assoc. Official Anal. Chem., 59 (1976) 894.

49. W.A. Ave., J. Chromatogr. Sci., 13 (1975) 329.

50. D.F. Natusch, T.M. Thorpe, Anal. Chem., 45 (1973) 1184A.

51. E.D. Pellizzari, J. Chromatogr., 98 (1974) 323.

52. H.A. McLeod, Anal. Chem., 47 (1975) 674.

53. H.P. Burchfield, D.E. Johnson, J.W. Rhoades, R.J. Wheller, J. Gas Chromatogr., 3 (1965) 28.

54. J. Connor, J. Chromatogr., 200 (1980) 15.

55. J. Connor, J. Chromatogr., 210 (1981) 193.

56. L.H. Keith, L.D. Ogle, A.E. Jones, R.C. Hanisch, R. C. Hall, A New GC Detector for TCDD and TCDF Analyses, Radian Corporation, Austin, TX, 1982.

57. C.F. Poole, J. High Resolut. Chromatogr. Chromatogr. Commun., 5 (1982) 454.

58. W.B. Knighton, E.P. Grimsrud, Anal. Chem., 55 (1983) 713.

59. J.A. Campbell, E.P. Grimsrud, L.R. Hageman, Anal. Chem., 55, (1983) 1335.

60. N.J. Dovichi, R.A. Heller, Anal. Chem., 55 (1983) 543.

61. S. Kapila, D.L. Bornhop, S.E. Manahan, G.L. Nickell, J. Chromatogr., 259 (1983) 205.

62. M. Hrivnac, Anal. Chem., 48 (1976) 937.

63. M.C. Bowman, M. Beroza, J. Chromatogr Sci., 9 (1971) 44.

64. J.K. Nelson, R.H. Getty, J.W. Birks, Anal. Chem., 55 (1983) 1767.

65. A.L. Lafleur, K.M. Mills, Anal. Chem., 53 (1981) 1202.

66. D.H. Fine, F. Rufel, D. Lieb, D.P. Rounbehlu, Anal. Chem., 47 (1975) 1188.

67. L.C. Thomas, A.K. Adams, Anal. Chem., 54 (1982) 2597.

68. A.K. Adams, D.L. Van Engelen, L.C. Thomas, J. Chromatogr., 303 (1984) 341.

69. R.P. Cooney, T. Vo-Dinh, J.D. Winefordner, Anal. Chim. Acta., 89 (1977) 9.

70. J.W. Robinson, J.P.Goodbread, Anal. Chim. Acta., 66 (1973) 239.

71. M. Zerezghi, K.J. Mulligun, J.A. Caruso, J.Chromatogr. Sci., 22 (1984) 348.

72. M.A. Eckhoff, T.H. Ridgway, J.A. Caruso, Anal. Chem., 55 (1983) 1004.

73. R.A. Heppner, Anal. Chem., 55 (1983) 2170.

74. S.R. Goode, B. Chambers, N.P. Buddin, Applied Spectro., 37 (1983) 439.

75. C.C. Greenwalt, K.J. Voorhees, J.W. Futrell, Anal. Chem., 55 (1983) 468.

76. J.H. Holland, C.G. Enke, J. Allison, J.T. Stults, J.D. Pinkston, B. Newcome, J.T.Watson, Anal. Chem., 55 (1983) 997A.

77. D. Rosenthal, Anal. Chem., 54 (1982) 63.

78. L. Eldjarm, E. Jellum, O. Stokke, Mass Spectro. Biochem. Med., (1972) 287.

79. P.T. Kissenger, Anal. Chem., 49 (1977) 448A.

80. T. Kojima, M. Ichise, Y. Seo, Anal. Chim. Acta., 101 (1978) 273.

81. R. Martin, Anal. Chem., 38 (1966) 1209.

82. D.M. Coulson, L.A. Cavanagh, J.E. Devries, B.J. Walther, Agric. Food Chem., 8 (1960) 399.

83. A. Liberti, Anal. Chim. Acta., 17 (1957) 247.

84. D.M. Coulson, J. Gas Chromatogr., 3 (1965) 134.

85. R.C. Hall, J. Chromatogr. Sci., 12 (1974) 152.

86. D.M. Coulson, L.A. Cavanagh, Anal. Chem., 32 (1960) 1245.

87. Equipment Manual, Dohrmann DE-20 Halogen Specific GC Detector, Dohrmann Envirotech (now Xertex), Santa Clara, CA.

88. T. Kojima, M. Ichise, Y. Seo, Bunseki Kagaku, 20 (1971) 20.

89. T. Kojima, M. Ichise, Y. Seo, Talanta, 19 (1972) 539.

90. T. Kojima, Y. Seo, J. Sato, Bunseki Kagaku, 23 (1974) 1974.

91. T. Kojima, M. Ichise, Y. Seo, Bunseki Kagaku, 24 (1975) 7.

92. D. Pirigner, M. Pascalau, J. Chromatogr., 8 (1962) 410.

93. G.G. Patchett, J. Chromatogr. Sci., 8 (1970) 155.

94. P. Jones, G. Nickless, J. Chromatogr., 75 (1973) 207.

95. J.F. Lawrence, J. Chromatogr., 87 (1973) 333.

96. W.P. Cochrane, B.P. Nilson, J. Chromatogr., 75 (1973) 207.

97. J.W. Dolan, R.C. Hall, Anal. Chem., 45 (1973) 2198.

98. J.F. Lawrence, A.H. Moore, Anal. Chem., 46 (1974) 755.

99. J.F. Lawrence, N.P. Sen, Anal. Chem., 47 (1975) 367.

100. G. Winnett, J. Chromatogr. Sci., 14 (1976) 255.

101. D.M. Coulson, J. Gas Chromatogr., 4 (1966) 285.

102. J.W. Rhoades, D.E. Johnson, J. Chromatogr. Sci., 8 (1970) 616.

103. W.P. Cochrane, B.P. Wilson, J. Chromatogr., 63 (1971) 364.

104. K.W. Davy, C.J. Morris, J. Chromatogr., 136 (1977) 361.

105. E. Von Rappard, G. Eisenbrand, R. Preussman, J. Chromatogr., 124 (1976) 247.

106. J. MacDonald, J.W. King, J. Chromatogr., 124 (1976) 364.

107. L.J. Carson, JAOAC, 66 (1983) 1335.

108. R.K. Goo, H.K. Inouye, H. Wakatsuki, Anal. Chem., 52 (1980) 1003.

109. O. Piringer, E. Wolff, J. Chromatogr., 284 (1984) 373.

110. Operations Manual, 700A Hall Electrolytic Conductivity Detector, Tracor Instruments, Inc., Austin, TX.

111. R.J. Anderson, The Hall Book, Tracor Instruments, Inc., Austin, TX.

112. R.J. Anderson, R.C. Hall, Am. Lab., 12, (1980) 108.

113. D.E. Johnson, C.G. Enke, Anal. Chem., 42 (1970) 329.

114. Environmental Protection Agency, Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations, Federal Register, Part III, 440 (233), Monday, December 3, 1979, pp. 69470, 69473.

115. W. Thornburg, Anal. Chem., 47 (1975) 157R.

116. S.P. Cram, R.S. Juvet, Jr., Anal. Chem., 48 (1976) 411R.

117. B.E. Pape, Clin. Chem., 22 (1976) 739.

118. L.S. Ettre, J. Chromatogr. Sci., 16 (1978) 396.

119. G. Zweig, J. Assoc. Official Anal. Chem., 61 (1978) 229.

120. S.O. Farwell, D.R. Gage, R.A. Kagel, J. Chromatogr. Sci., 19 (1981) 358.

121. R. Otson, D.T. Williams, Anal. Chem., 54 (1982) 942.

122. T.B. Gibb, P.H. Wolfe, J. Chromatogr. Sci., 20 (1982) 471.

123. G.F. Ernst, J.B. VanLierop, J. Chromatogr., 109 (1975) 439.

124. D.J. Hallett, R.J. Norstrom, F.I. Onuska M.E. Comba, R. Sampson, J. Agric. Food Chem., 24 (1976) 1189.

125. H.L. Crist, R.F. Moseman, J. Chromatogr., 160 (1978) 49.

126. R. Otson, D.T. Williams, J. Chromatogr., 212 (1981) 187.

127. M.A. Juke, J.E. Froberg, G.M. Doose, H.T. Masumoto, J. Assoc. Official Anal. Chem., 64 (1981) 1187.

128. C.P. Nulton, C.L. Haile, D.P. Redford, Anal. Chem., 56 (1984) 598.

129. D. Reichert, U. Spengler, D. Henschler, J. Chromatogr., 179 (1979) 181.

130. S. Sagg, R.J. Steger, J. Chromatogr., 238 (1982) 121.

131. B.E. Pape, M.A. Ribick, J. Chromatogr., 136 (1977) 127.

132. R.C. Hall, C.A. Risk, J. Chromatogr. Sci., 13 (1975) 519.

133. C.A. Risk, R.C. Hall, J. Chromatogr. Sci., 15 (1977) 156.

134. G. Yip, J. Chromatogr. Sci., 13 (1975) 225.

135. K.W. Kirby, J.E. Keiser, J. Groene, E.F. Slach, J. Agric. Food Chem., 27 (1979) 757.

136. J.C. Escalier, C. Bellet, J. Chromatogr., 167 (1978) 125.

137. D.W. Westerman, S.S. Katti, M.W. Vogelzary, C.L. Li, B.C. Gates, L. Petrakis, Fuel, 62 (1983) 1376.

138. F.J. Sena, L.C. Croce, J. Chromatogr. Sci., 20 (1982) 575.

139. J.H. Phillips, R.J. Coracor, S.R. Prescott, Anal. Chem., 55 (1983) 889.

140. R.G. Schiller, R.B. Bronsky, J. Chromatogr. Sci., 15 (1977) 541.

141. B.J. Ehrlich, R.C. Hall, R.J. Anderson, H.G. Cox, J. Chromatogr. Sci., 19 (1982) 245.

142. M. Galoux, J.C. VanDamme, A. Bernes, J. Potviu, J. Chromatogr., 177 (1979) 245.

143. R.J. O'Connell, A.G. Singer, F.L. Stern, S. Jesmajian, W.C. Agosta, Behavioral Neural Biol., 31 (1981) 457.

144. A.G. Singer, R.J. O'Connell, F. Macrides, A.F. Bencsatt, W.C. Agosta, Physiol. Behavior, 30 (1983) 139.

145. S. Gluck, J. Chromatogr. Sci., 20 (1982) 103.

146. A.D. Sauter, L.D. Betowski, T.R. Smith, V.A. Strickler, R.F. Beimer, B.N. Colby and J.E. Wilkinson, J. High Resolut. Chromatogr. Chromatogr. Commun., 4 (1981) 366.

147. C.J. Kirchmer, M.C. Winter and B.A. Kelly, Environ. Sci. Technol., 17 (1983) 396.

148. V. Lopez-Avila and R. Northcutt, J. High Resolut. Chromatogr. Chromatogr. Commun., 5 (1982) 67.

149. A.J. Bard and L.R. Falkner, Electrochemical Methods, John Wiley and Sons, New York, 1980, p.65.

150. O. Popovych and R.P.T. Tomkins, Nonaqueous Solution Chemistry, John Wiley and Sons, New York, 1981, Ch.7.

151. G.D. Christian, Analytical Chemistry, 3rd edition, John Wiley and Sons, New York, 1980, p.486.

152. R.C. Weast, CRC Handbook of Chemistry and Physics, 61st edition, CRC Press, Boca Raton, FL, 1980-1981.

153. M.G. Natrella, Experimental Statistics, National Bureau of Standards, Handbook 91, U.S. Government Printing Office, Wash., D.C., 1966, p.2-2 and Ch.5,6.

154. D.A. Kurtz, Anal. Chim. Acta, 150 (1983) 105.

155. W.J. Blaedel, D.G. Iverson, Anal. Chem., 48 (1976) 2027.

156. D.L. Massart, A. Dijkstra and L. Kaufman, Techniques and Instrumentation in Analytical Chemistry, Vol I, p.9. Evaluation and Optimization of Laboratory Methods and Analytical Procedures, Techniques and Instrumentation in Analytical Chemistry, Elsevier Scientific Publishing Co., 1978, pg. 292.

157. R.B. Dean and W.J. Dixon, Anal. Chem., 23 (1951) 636.

158. F.W. McLafferty, Interpretation of Mass Spectra, 3rd edition, University Science Books, Mill Valley, CA, 1980, Ch.2,3.

159. J.S. Garden, D.G. Mitchell, W.N. Mills, Anal. Chem., 52 (1980) 2310.

160. J. Agterdenbos, Anal. Chim. Acta., 108 (1979) 315.

161. N.R. Draper, H. Smith, Applied Regression Analysis, 2nd edition, John Wiley and Sons, New York, 1981, p.221.

162. G.W. Snedecor, W.G. Cochran, Statistical Methods, 7th edition, The Iowa State Press, Ames, Iowa, 1980, p.291.

163. B. Ostle, R.W. Mensing, Statisics in Research, 3rd edition, The Iowa State Press, Ames, Iowa, 1975, p.353.

164. B.P. Wilson, W.P. Cochrane, J. Chromatogr., 106 (1975) 174.

165. B.E. Pape, D.H. Rodgers, T.C. Flynn, J. Chromatogr., 134 (1977) 1.

166. W.G. Cochran, G.M. Cox, Experimental Designs, 2nd ed, John Wiley & Sons, NY, 1957, p. 347.

167. W. Mendenhall, Introduction to Linear Models and the Design and Analysis of Experiments, Wadsworth Publishing Co., Inc., Belmont, Calif, 1968, pg. 287.

168. I.B. Rubin, T.J. Mitchell, G. Goldstein, Anal. Chem., 43 (1971) 717.

169. C.R. Hicks, Fundamental Concepts in the Design of Experiments, 3rd ed, Holt, Rinehart and Winston, NY, 1982, p. 340.

170. P.W.M. John, Statistical Design and Analysis of Experiments, The MacMillan Co., NY, 1971, pg. 204.

171. G.H. Dodo, S.J. Hawkes, L.C. Thomas, J. Chromatogr., in press.

172. A. Zlathis, D.C. Fenimore, L.S. Ettre, J.E. Purcell, J. Gas Chromatogr., 3 (1963) 75.

173. C.C. Neto, J.T. Koffer, J.W. DeAlancar, J. Chromatogr., 15 (1964) 301.

174. S. Nygren, P.E. Mattsson, J. Chromatogr., 123 (1976) 101.

175. S. Nygren, J. Chromatogr., 142 (1977) 109.

176. F. Poy, Chromatogr. Symp. Ser., 1 (1979) 187.

177. J.D. Kelley, J.Q. Walker, Anal. Chem., 41 (1969) 1340.

178. S. Wicar, J. Chromatogr., 295 (1984) 395.

179. S. Wicar, J. Chromatogr., 298 (1984) 373.

180. G.H. Dodo, T.L. Ramus, L.C. Thomas, J. Chromatogr., in press.

181. N.W. Davies, Anal. Chem., 56 91984) 2602.

182. R. Wenske, personal communication, Tracor Instruments, Inc., Austin, TX, May 1985.

APPENDICES

Appendix A

List of Abbreviations

A_i	peak area for internal standard
A_r	peak area for analyte reference compound
A_{rs}	peak area for response standard
A_s	peak area for analyte external standard
A_u	peak area for analyte in sample
A_{u+s}	peak area for unknown analyte plus added analyte standard in sample
AC	alternating current
ADC	analog to digital converter
AIM	AIM microcomputer
AMP	amplifier
ARM	analyte reference material
b	y-intercept for curve
b_L	y-intercept for log-log curve
CB	chlorobenzene
CM	calibration material
CRM	certified reference material
DCB	dichlorobenzene
DCPeA	1,5-dichloropentane
ECD	electron capture detector
ElCD	electrolytic conductivity detector
ES	external standard method
eV	electron volt
F_d	detector volumetric flow rate

f_{ES}	instrumental response factor in ES method
f_{IS}	instrumental response factor in IS method
f_r	instrumental response factor for analyte reference compound
f_{RFC}	instrumental response factor in RFC methods
FID	flame ionization detector
FR	measured mass flow value
GC	gas chromatography
GC-HECD reactor-MS	gas chromatograph interfaced to a mass spectrometer through the high temperature reactor of a HECD
GC-MS	gas chromatography - mass spectrometry
GC-reactor-MS	same as GC-HECD Reactor-MS
HCBD	hexachlorobutadiene
HCCHA	β-hexachlorocyclohexane
HCCPD	hexachlorocyclopentadiene
HCl	hydrogen chloride
HECD	Hall electrolytic conductivity detector
ID	inner diameter
IOS	internal organization for standardization
IS	internal standard method
k	number of factors in a factorial experiment
$k_\#$	specifies a particular factor
L	differential conductance signal
L_o	baseline differential conductance signal

L_{RCl}	differential conductance signal due to analyte, RCl_N
L_T	total differential conductance signal
LOD	limit of detection
m	slope of curve
M_i	mass of internal standard
m_L	slope of log-log curve
M_r	mass of analyte reference compound
M_s	mass of analyte external standard
M_u	unknown mass of analyte in sample
MW_{rs}	molecular weight of the response standard
MW_u	molecular weight of the analyte of interest
M/z	mass to charge ratio
N	number of atoms of a particular element per molecule
n	number of data points or trials in an experiment
N_C	number of carbon atoms per molecule
N_{Cl}	number of chlorine atoms per molecule
N_O	number of oxygen atoms per molecule
N_{rs}	number of simple species equivalents per response standard molecule
N_u	number of simple species equivalents per analyte molecule
NBS	national bureau of standards
OD	outer diameter
P	total column plate number
p	number of parameters
PCB	polychlorinated biphenyl

PCEA	pentachloroethane
Q	number of levels in a factorial experiment
Q_b	base point level in a factorial experiment
Q_0	lowest level in a factorial experiment
Q_1	highest level in a factorial experiment
RFC	response factor calibration
RM	reference material
RSD	relative standard deviation
s	standard deviation
SA	standard addition method
SCM	standard calibration material
S/N	signal to noise ratio
SRM	standard reference material
t_R	analyte retention time
TCAn	2,4,6-trichloroaniline
TCB	1,2,4-trichlorobenzene
TCPrA	1,2,3-trichloropropane
TCT	α,α,α-trichlorotoluene
TIC	total ion chromatogram
TM	test material
Vc	cell volume
V_d	detector volume
V_G	total HECD analyte gas volume
V_L	total HECD analyte liquid volume
w	confidence interval at 100(1-α)% confidence level
x	an independent variable in a polynomial function

X_{rs}	equivalents of simple species for the response standard in the sample of interest
X_u	unknown equivalents of simple species for the analyte in the sample of interest
y	dependent variable in a polynomial function
Yhat	expected value of Y for a particular data point from a multiple regression
Z	moles of a compound
Z_u	moles of analyte in sample solution
1COA	1-chlorooctane
2CN	2-chloronaphthalene
α	confidence level is $100(1-\alpha)\%$
β_1	a multiple regression parameter
Δt	change in time
λ_1	equivalent ion conductivity for ion, i
ℓ/A	cell constant
θ	$\theta \cdot 100\%$ = percent increase in column peak widths
θ_G	$\theta_G \cdot 100\%$ = percent increase in column peak widths due to V_G
θ_L	$\theta_L \cdot 100\%$ = percent increase in column peak widths due to V_L

Appendix B

Alterations Made to the Tracor 700A Hall Electrolytic Conductivity Detector and the Tracor 560 Gas Chromatograph

Tracor Model 700A Hall Electrolytic Conductivity Detector

1. An aluminum block had to be machined for adapting the HECD reactor to the Tracor Model 560 GC. There was insufficient room in the normal detector region of the Tracor 560 GC to allow placement of the base heating element and thermocouple in the installed reactor base. The aluminum block enclosed the base heater region and provided locations to insert the heating element and thermocouple sensor.
2. The signal output amplifier for the HECD differential conductance signal was replaced with an AD522 instrumentation amplifier. The AD522 rejects common-mode noise from the amplified output signal. Excessive common-mode noise had been observed, probably due to fluctuations in the main heating element common voltage, which was inadvertently grounded to the instrument chassis.
3. The potentiometer used for signal output fine adjustment developed a discontinuity. The potentiometer was replaced by a voltage divider circuit.

Tracor Model 560 Gas Chromatograph

1. Excessive noise in the instrument ground potential was a problem, producing noise in the amplified output signal. A passive line filter unit was installed to reduce voltage surges and spikes in the AC line.
2. The ground potential noise persisted and appeared to coincide with the switching of power to instrument heaters. Thus, separate AC lines from the passive filter unit were used to provide power for the high current heaters and the GC transformer. The GC transformer provided AC power for all GC power supplies.
3. Further troubleshooting revealed the main heater element common to be inadvertently contacting the instrument chassis. The high current heating element was dumping AC common potentials into the instrument ground. Correcting this inadvertent contact corrected the instrument ground noise problem. It is likely that this problem lead to the first and second attempts to correct fluctuating ground voltages for the Tracor 560 GC, and the installation of an AD522 output instrumentation amplifier.
4. Filter capacitors used in all three power supplies in the Tracor 560 GC failed during a three year period. The cause is not known. However, all of the replacement capacitors had higher AC voltage ratings, and have worked flawlessly since installation. The $\pm$ 15 V, 5 V power supply, $\pm$ 300 V, $\pm$600 V

power supply, and the 60 V power supply all required capacitor replacement.

5. The solid state triac which controls the main heater element switch failed intermittently. The triac was replaced.
6. A Logic memory component which stored the temperature programming parameters failed and the component was replaced.
7. Heat from the main oven, two flash vaporization injectors, two detector blocks, and the HECD high temperature reactor raise the temperature in the detector area where the differential conductivity cell is located. Insulation was placed in the detector region, and between the HECD high temperature reactor and the differential conductivity cell. An air circulation fan was also placed in the detector area. These measures reduced temperatures near the differential conductivity cell.
8. An On-column injection system for capillary columns was installed in the Tracor 560 GC. The system included a column head pressure regulator, precision flow controller, and a SGE On-column injector. The SGE On-column injector allows the tip of a fused silica injection needle to be inserted approximately 1 in. into a fused silica capillary column. A pneumatically controlled seal allows needle placement for injection and subsequent needle removal while column carrier gas flow is maintained. The seal must be replaced following approximately 25 injections to maintain leak-free operation. The injector is cooled by air flow through the injector base region where the injector enters the oven. The flash vaporization injectors are not heated during on-column injector usage.

Appendix C

Evaluation of Noise in the Hall Electrolytic Conductivity Detector

The identification of noise sources in the HECD can be challenging since noise can arise form many different locations and for many different reasons. The HECD should first be detached from the chromatographic column, and evaluated to confirm that the observed problems are arising from the detector. Poor HECD operation can result in increased baseline noise and peak tailing, or erratic output signals. The most successful procedure to evaluate noise in the HECD and identify noise sources is to isolate detector components and observe the HECD output signal:

1. The transfer tube is first disconnected at the differential conductivity cell and replaced by a plug. The output signal is monitored with the HECD solvent loop isolated from other HECD components. Usually, the isolated solvent loop will yield a normal output signal.
2. If the output signal for the isolated solvent loop configuration is noisy, several sources of noise are likely. The electronics can be evaluated by removing the cell excitation connection. At this point the output signal should include very little noise. Reconnect the cell excitation signal. Air leakage around the reference cell electrode will produce intermittent output signal spikes. Air leakage will result in bubbles in the solvent waste exit, and leakage can be confirmed by placing a small amount of n-propanol around the teflon

insulator at the reference electrode. If a poor signal persists at this point and the pump is functioning normally (the pump should never be allowed to run in the absence of solvent), then the differential conductivity cell must be cleaned and the resin replaced.

3. Replacing the ion-exchange resin and cleaning the cell should be considered a last step. Typically, resin replacement is required at only 6 to 9 month intervals. A very successful procedure for cell cleaning is provided in the HECD operations manual along with information on resin replacement [48]. If peak tailing has been a problem then more acidic resin should be used, however, excessive acidic resin will produce high baseline noise levels.
4. When the isolated solvent loop is properly functioning, then the gas phase regions of the HECD should be evaluated. Hydrogen and helium gases of low purity can cause detector noise, but Airco, grade 4.5 gases with hydrocarbon traps have worked well. If the detector had been functioning properly earlier, then the gases are probably sufficiently pure unless the traps need to be replaced. Usually the HECD requires maintenance due to nickel catalyst failure. Carbonaceous material on the nickel surface can render the catalyst ineffective. The nickel tubing should be replaced with high purity Ni-200, and the Teflon transfer tube should be washed with methanol and dried. Cleaning spent nickel tubing has not been attempted in these experiments since purchase prices for nickel tubing are reasonable. After conditioning the new

catalyst at high temperature in a hydrogen atmosphere, the transfer tube can be reattached to the differential conductivity cell, and the output signal evaluated.

5. Once detector output is functioning properly, then the chromatographic column can be attached to the HECD.

HECD operation generally requires more maintenance than other GC detector systems, however, the unique advantages of HECD measurements may justify use of this detector.

Appendix D

Data Analysis Computer Program Used for Response Factor Calibration Calculations, Control Composite Factorial Experimental Calculation and Multiple Regression Analysis

Computer Program Description

The following computer program was written and developed to provide rapid, flexible data analyses for laboratory experiments. The program, as listed herein, emphasizes calculations for data collected during this thesis research. Specialized calculations are included for response factor calibration and central composite factorial experiments. However, other calculations could easily be included, using the already developed set of functions.

The program is written in "C" language for the IBM PC version, Lattice "C" compiler. "C" language was chosen due to the language's flexibility, structured and readable programming style, production of efficient executable code, implementation of double precision calculations, and utilization of the 8087 coprocessor. A matrix oriented data structure was utilized where columns generally represent different variables while rows represent individual data points.

Dynamically allocated data matrix memory structures are an example of the language flexibility. The "C" language functions which allocate memory for the matrix structure, pointers and matrix elements are mx_create(), mx_alloc_struct() and mx_mem_alloc().

Memory space is released by mx_erase(). These functions appear at the end of the following program listing.

The program executes calculations on user defined data matrices by a series of menu choices. The master menu function, choose(), provides nine choices. Choice 9 exits from the program to the DOS operating system.

The first choice, data management, executes the choose_data() function for data entry, editing and transformation. The user specifies the number of rows and columns for the matrix at the time of data entry, using the mx_enter() function. Matrices can be edited and catenated after matrix formation via choices in the choose_edit() function. Data contained in the matrices can be transformed by scalar addition and multiplication, or via functions which include inverse, square root, power, exponential, logarithmic, and trigonometric transformations from the choose_ transform() function. Finally, elementwise functions allow addition, subtraction, multiplication and division of corresponding data elements within two matrices of equal dimensions, and matrix multiplication, transposition or inversion are provided from the choose_matrix_op() function. Detailed listings of these functions were not included in this appendix due to space limitations, however, the listings are available upon request.

Master menu choice 8 executes choose_fdisk() with options for data output to the console and printers, disk file access, and file manipulation e.g., list, copy, rename, and erase. Lotus 1-2-3 compatible files for subsequent plotting can be produced. These detailed functions are not listed in this appendix.

Multiple Regression. Choice 3 from the master menu executes choose_regress(). This function requests the file names for an X-matrix, Y-matrix, and optional weight matrix. The weighting matrix is handled within the get_weight_mat() function.

The multiple regression is accomplished by multiplying the X-matrix and Y-matrix by the transpose X-matrix to produce the N-matrix and Q-matrix, respectively. Next the inverted regression matrix, I-matrix, is formed by inverting the N-matrix. Finally, the I-matrix is multiplied by the Q-matrix to produce the parameter matrix, B-matrix. In summary $N = X'X$, $Q = X'Y$, $I = (X'X)^{-1}$ and $B = (X'X)^{-1} X'Y = I \cdot Q$ [161]. The function mx_regress() performs these operations.

After completing the multiple regression calculations, data is output to an ASCII-coded disk file, and the choose_regression menu is reached. Choice 2 of the choose_regression menu provides a table for file output of X values, Y values, Yhat values, and residuals.

The regression function is also capable of auto-polynomial regression. The user enters a first order X-matrix and Y-matrix and the program performs an analysis of variance. A new column is added to the X-matrix to increase the polynomial order by one after each regression pass. The procedure continues, increasing the polynomial order, until Fcalc is less than Fvalue or the available degrees of freedom become too small. After each regression pass, data is output to a separate disk file for later perusal.

Response Factor Calibration Calculations. The rfc() function is executed by choosing 4 from the master menu. The rfc() function asks the user to enter a 4 character data set code, XXXX, which identifies the four required single column input files. anaXXX contains the analyte peak areas, rsaXXXX contains the response standard peak areas, amwXXXX contains analyte molecular weight, and ancXXXX contains the number of chlorine atoms per analyte molecule for each data point. The user is also prompted for the response standard concentration, molecular weight and number of chlorine atoms per molecule for the analysis. Following RFC calculations, seven output files are produced. The files contain response ratio, log of response ratio, response factor, analyte organochlorine concentration, log of analyte organochlorine concentration, analyte mass concentration, and a summary table. Selected output files can be formatted and used in the multiple regression function.

Central Composite Factorial Experiment Calculations. Choice 5 for the master menu executes the cen_comp_exp() function which prepares an X-matrix and Y-matrix for multiple regression from factor values and response values obtained in a factorial experiment. The subsequent multiple regression produces a response surface function. The user indicates the number of factors to be evaluated and the order of the response surface. Each set of factor values is placed in a single matrix column file called fac#XXXX where XXXX is the data set code specified by the user. The #, a single digit numeral, indicates which factor is contained in the file. The user is also prompted for the inclusion of

second-order interaction parameters. Three output files are produced including two files containing the X-matrix and yyyXXXX containing the Y-matrix. These two files can be used in the multiple regression function to obtain a response surface function and important regression data. The third file contains a summary table.

"C" Program Listing

The following program listing contains the important functions used for the Data Analysis Computer Program. Functions which execute data output, matrix calculations and file utilities are not included due to space limitations. However, these functions are available upon request.

```
/* DATAANL.C   -     The following computer programs are implemented by
*                 choosing operations to be performed from a set of menus.
*                 All data manipulations use double precision arithmetic.
*                 Disk file storage for data which may be used in later
*                 calculations is also double precision.  Data intended
*                 for future output is stored in ascii coded disk files.
*                 The programs are designed to be flexible, but not always
*                 user friendly.
*                    The programs are designed to manipulate data sets
*                 contained within matrices.  Generally, columns represent
*                 values for different variables while rows represent values
*                 for different data points.  The matrices are dynamically
*                 allocated, and an individual matrix does not have specific
*                 storage limitations.
*                    These programs were written for performing calculations
*                 on experimental data collected from a GC-HECD instrument.
*                 Specialized programs include calculations for multiple
*                 regression, response factor calibration, and central
*                 composite factorial experimental data.  Additionally, the
*                 data manipulation section allows general data calculations
*                 to be performed.
*
*
*     01 April 1985          by  Terry L. Ramus
*
*     Compiling and linking DATAANL.C to form DATAANL.EXE requires object code
*     file DATAOBJ.OBJ and library files CLIB.LIB.  These files contain selected
*     program functions written for DATAANL.C.  The Lattice "C" compiler,
*     the Corona LINK, and a Corona-PPC portable PC computer were used for
*     program development.  The programs are general for the IBM PC, except for
*     the clear_screen() and pause() functions.
*
*/

#include <stdio.h>     /*  HEADER files used by the compiler are listed  */
#include <stdtyp.h>
#include <math.h>
#include <msdos.h>

#define SIZEDEC  80    /*  Define constant, SIZEDEC, to be 80  */
#define SIZELINE  95   /*  Define constant, SIZELINE, to be 95  */
#define clear_screen() (cputs("2J"))   /*  Operation to clear screen  */

/*  Global Storage Area  */
char file_root[16] = "test";
char out_root[16] = "testout";
char bin_end[6] = ".mat";
char asc_end[6] = ".asc";
char gen_end[6] = ".xxx";
char lotus_end[6] = ".prn";
int m_rows, m_cols;
long yymmdd;    /* clock  [0] year, [1] month,   [2] day,     [3] weekday     */
```

```
short clock[8]; /* clock  [4] hour, [5] minutes, [6] seconds, [7] hundredths  */

/*  Functions which return parameters are listed here  */
matrix mxr_extract(), mxc_extract(), mxr_cat(), mxc_cat(), *mx_regress();
matrix mxr_replace(), mxc_replace(), mxr_delete(), mxc_delete(), mx_erase();
matrix mx_create(), mx_alloc_struct(), mx_mem_alloc(), mx_copy(), mx_read();
matrix mx_log_choose(), mx_pow_choose(), mx_exp_choose(), mx_trig(), mx_one();
double mean(), max_value(), min_value(), variance(), std_dev();
double covariance(), correlation(), mx_get_element();
char *xcgets();
matrix mx_2_mat(), get_weight_mat(), mx_mul_elementwise(), mx_div_elementwise();
matrix mx_log10_elementwise(), mx_ln_elementwise(), mx_pow_elementwise();
matrix mx_inv_elementwise(), mx_sqrt_elementwise(), mx_exp_elementwise();
matrix mx_exn_elementwise();
char *prompt_work_file(), *prompt_out_loc(), *prompt_xout_file(), *prompt_sec_file();
char *comment(), *file_list();
/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
main()
{
    time(clock);   /*  Set time and date  */
    yymmdd = (long)10000 * (clock[0] - 1900) + 100 * clock[1] + clock[2];
    choose();      /*  Enter MASTER MENU  */

    /*  end of main  */
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose()
/*  MASTER MENU function.  Choose option #9 to EXIT MENU */
/*  Enter multiple regression, response factor calibration, and central
*   composite factorial calculations from this menu */
/*  Enter file management and data management menus from here */
{
    char *pc;              /* pointer to a char string */
    char hline[SIZEDEC];   /* Character string for input */
    short yy, mm, dd;

    for (;;)
        {
        clear_screen();
        cprintf("\n %s \n", ctime(clock));
        cputs("\nMAIN MENU OPTIONS ARE:\n");
        cputs(" 1  Data Management (Enter, Edit, Scalar, Elementwise and Matrix Operations).\n");
        cputs(" 2  .\n");
        cputs(" 3  Linear Regression (Polynomial and Multiple).\n");
        cputs(" 4  RFC Calculation (Uses anaCode, rsaCode, amwCode and ancCode FILES).\n");
        cputs(" 5  Center Composite Experiment calculation (Uses fac#Code and respCode FILES).\n");
        cputs(" 6  .\n");
        cputs(" 7  .\n");
        cputs(" 8  File Management (List, Rename, Copy, Erase, Plot, Print).\n");
        cputs(" 9  EXIT.\n");
```

```
        cputs("\n  Your choice?  ");
        pc = xcgets(hline, SIZELINE);        /* read input */
        cputs("\n");
        switch (*pc)        /* Execute CASE instructions which match *pc, 1-9 */
            {
        case '1':
            choose_data();
            break;
        case '2':
            break;
        case '3':
            choose_regress();
            break;
        case '4':
            rfc();
            break;
        case '5':
            cen_comp_exp();
            break;
        case '6':
            break;
        case '7':
            break;
        case '8':
            choose_fdisk();
            break;
        case '9':
            return(0);        /* EXIT from choose() function to DOS */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
}
/* end of choose() */

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_data()
/*  DATA management menu */
{
    char *pc;     /* pointer into a char string */
    char hline[SIZEDEC];

    for (;;)
        {
        clear_screen();
        cputs("DATA MENU OPTIONS ARE:\n");
        cputs(" 1  SELECT working data FILENAME.\n");
        cputs(" 2  ENTER new data (Create new File).\n");
        cputs(" 3  EDIT existing data.\n");
        cputs(" 4  SCALAR and FUNCTION OPERATIONS on existing data.\n");
```

```
        cputs(" 5  ELEMENTWISE and MATRIX OPERATIONS on existing data.\n");
        cputs(" 6  .\n");
        cputs(" 7  LIST disk files.\n");
        cputs(" 8  PRINT a BINARY file.\n");
        cputs(" 9  RETURN to MAIN menu.\n");
        cputs("\n  Your choice?  ");
        pc = xcgets(hline, SIZELINE);        /* read input */
        cputs("\n");        /* to move cursor to next line */
        switch (*pc)
            {
        case '1':
            mx_main_name();
            break;
        case '2':
            mx_enter();
            break;
        case '3':
            choose_edit();
            break;
        case '4':
            choose_transform();
            break;
        case '5':
            choose_matrix_op();
            break;
        case '6':
            break;
        case '7':
            file_list();
            break;
        case '8':
            mx_bin_display();
            break;
        case '9':
            return(0);        /* exit to MAIN MENU */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
    /* end of choose_data()  */
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_regress()
/*  Perform MULTIPLE REGRESSION and enter REGRESSION MENU */
/*  Regression requires an X-matrix and Y-matrix, optionally a weight matrix */
/*  Performs multiple or polynomial linear least squares regression
*       Y-matrix (can use any name)       1 column, n rows of n data points
*       X-matrix (can use any name)       2 columns, n rows of n data points
*             column 1  ---  contains n ones
```

```
*            column 2  ---  contains n data points
*/
/*  Program allows auto-polynomial regression to find the best order */
/*  Outputs up to three types of ascii files:
*       ???????# ..................  regression data, important sums
*       ???????v ..................  auto-regression, analysis of variance table
*       ???????r ..................  regression residuals
*/
{
    char hline[SIZEDEC];    /*  character strings */
    char xout_file[16];
    char view_file[16];
    char title[SIZEDEC];
    char date[SIZEDEC];
    char *pc, pcpoly;
    char ascii[10];
    char x_mat_name[16], y_mat_name[16], temp_file[16];
    char head[125];
    int xrow, xcol, yrow, ycol, err_row, err_col, i, j, df, poly_order, order_max;
    int count;       /* integer variables */
    extern int m_rows, m_cols;     /* externally defined variables */
    matrix *mat_ptr, mattemp1, mattemp2;    /* pointers to matrix structures */
    matrix x_mat, y_mat, err_mat, matn, matq, matni, matB;
    static double ss_dtr, yhat, residual, ss_y, fvalue, ci_bt, xvalue, var_cur;
    static double std_b, ci_bi, tvalue, fcalc, ss_prior, sum_yw, sum_w, mean_yw;
    static double resid_sum, resids_sum, sum_reg, sum_regs, sum_x, sum_xw;
    static double sum_xws, sum_y, sum_yws, sum_xyw, mean_xw, mean_x, mean_y, sxx;
    static double syy, sxy, sy, err;      /* double precision variables */

    FILE *fpname;        /* file pointers */
    FILE *fpview;

    clear_screen();
    cprintf("Enter X-MATRIX filename (%s is appended), <RETURN> :\n",
    bin_end);
    xcgets(hline, SIZELINE);
    strncpy(x_mat_name, hline, 9);
    strcat(x_mat_name, bin_end);
    cprintf("\nX-MATRIX file is: %s\n\n", x_mat_name);
    x_mat = mx_read(x_mat_name, title, date);
    xrow = m_rows;      /* number of rows */
    xcol = m_cols;      /* number of columns */

    cprintf("Enter Y-MATRIX filename (%s is appended), <RETURN> :\n",
    bin_end);
    xcgets(hline, SIZELINE);
    strncpy(y_mat_name, hline, 9);
    strcat(y_mat_name, bin_end);
    cprintf("\nY-MATRIX file is: %s\n\n", y_mat_name);
    y_mat = mx_read(y_mat_name, title, date);
    yrow = m_rows;      /* number of rows */
    ycol = m_cols;      /* number of columns */
```

```
err_mat = get_weight_mat(x_mat);   /* function to input weight matrix */
err_row = m_rows;   /* number of rows */
err_col = m_cols;   /* number of columns */

cputs("\nDo you want the program to find the best Polynomial Fit ? \n");
cputs("(Y or N) ?   ");
pc = xcgets (hline, SIZELINE);
cputs ("\n");
pcpoly = tolower(*pc);
if(pcpoly == 'y')    /* maximum order for auto-regression */
    {
    cprintf("\nInput the Maximum Order for the Polynomial Fit ? ");
    xcgets(hline, SIZELINE);
    sscanf(hline, "%d", &order_max);
    }
else
    order_max = 1; /* maximum order is 1 if auto-regression is not requested*/
cputs ("\n\n");
strcpy(out_root, "reg");
strncpy(temp_file, prompt_xout_file(), 7);
strcpy(view_file, temp_file);
strcat(view_file, "v");
strcpy(out_root, view_file);
strcat(view_file, asc_end);  /* character string for auto-regression output file */
strcpy(title, "\"");    /* quote marks around characters -- lotus compatible */
strcat(title, comment());
strcat(title, "\"");
strcpy(date, "\"");
strcat(date, ctime(clock));   /* output date and time to file */
strcat(date, "\"");

/* ... Regression begins here ..................................... */

for(poly_order = 1, count = 0; poly_order <= order_max; poly_order++)
    {
    mat_ptr = mx_regress(x_mat, y_mat, err_mat); /* do regression */
    matn = *(mat_ptr);
    matq = *(mat_ptr + 1);
    matni = *(mat_ptr + 2);   /* inverted regression matrix */

    matB = *(mat_ptr + 3);    /* parameter regression matrix */

    df = x_mat->rows - x_mat->cols;
    /* calculate important sums */
    for (i = 0, sum_yw = 0, sum_w = 0; i < x_mat->rows; i++)
        {
        if (err_mat == MXEMPTY || y_mat->rows != err_mat->rows)
           err = 1.0;
        else
           err = *(*(err_mat->element+i)+i);
        sum_yw += err * *(*(y_mat->element+0)+i);
```

```
    sum_w += err;
    }
mean_yw = sum_yw / sum_w;
for (i = 0, resid_sum = 0, resids_sum = 0, sum_reg = 0, sum_regs = 0, sum_x = 0, sum_xw = 0,
    sum_xws = 0, sum_y = 0, sum_yws = 0 ,sum_xyw = 0; i < x_mat->rows; i++)
    {
    for (j = 0, yhat = 0; j < x_mat->cols; j++)
        yhat += *(*(matB->element+0)+j) * *(*(x_mat->element+j)+i);
    if (err_mat == MXEMPTY || y_mat->rows != err_mat->rows)
       err = 1.0;
    else
       err = *(*(err_mat->element+i)+i);
    resid_sum += *(*(y_mat->element+0)+i) - yhat;
    resids_sum += (*(*(y_mat->element+0)+i) - yhat) * (*(*(y_mat->element+0)+i) - yhat);
    sum_reg += *(*(y_mat->element+0)+i) - mean_yw;
    sum_regs += (*(*(y_mat->element+0)+i) - mean_yw) * (*(*(y_mat->element+0)+i) - mean_yw);
    sum_x += *(*(x_mat->element+1)+i);
    sum_xw += err * *(*(x_mat->element+1)+i);
    sum_xws += err * *(*(x_mat->element+1)+i) * *(*(x_mat->element+1)+i);
    sum_y += *(*(y_mat->element+0)+i);
    sum_yws += err * *(*(y_mat->element+0)+i) * *(*(y_mat->element+0)+i);
    sum_xyw += err * *(*(x_mat->element+1)+i) * *(*(y_mat->element+0)+i);
    }
mean_xw = sum_xw / sum_w;
mean_x = sum_x / sum_w;
mean_y = sum_y / sum_w;
sxx = sum_xws - sum_xw * sum_xw / sum_w;
syy = sum_yws - sum_yw * sum_yw / sum_w;
sxy = sum_xyw - sum_xw * sum_yw / sum_w;
sy = sqrt((syy - sxy * sxy / sxx)/ df);

/* ... Analysis of Variance Begins Here -- Auto-regression ......,.....*/
if(pcpoly == 'y')
    {
    /* do only during first pass through loop */
    if (poly_order <= 1)
        {
        clear_screen();
        fpview = fopen (view_file, "w");  /* open file for output */
        /* output information to analysis of variance table file */
        fputs(title, fpview);
        fputs("\n", fpview);
        fputs(date, fpview);
        sprintf(hline,"\n\n                    \"ANALYSIS OF VARIANCE TABLE\"\n");
        fputs(hline, fpview);
        fputs(hline, stdout);
        strcpy(head, "\n\"Od\" \"n\"  \"p\"  \"df\" \"Sum of Sq\" \"Mean Sqr\"
            \"Redu.,Bi\"  ");
        strcat(head, "\"__Fcalc_\"  \"F(al,1,df)\"\n\n");
        fputs(head, fpview);
        fputs(head, stdout);
        sprintf(hline,"\"--\" %3.0d    0  %3.0d %11.4lg %11.4lg        \"--\"
```

```
            \"--\"    \"--\"\n", x_mat->rows, x_mat->rows, sum_yws, sum_yws / x_mat->rows);
        fputs(hline, fpview);
        fputs(hline, stdout);
        cprintf("Input F-value for (1, %d, 1-alpha) for order 0 ? ", x_mat->rows - 1);
        xcgets(hline, SIZELINE);
        sscanf(hline, "%lf", &fvalue);
        /* calculate F-value for zero order case */
        fcalc = (sum_yws - sum_regs) / (sum_regs / (x_mat->rows - 1));
        sprintf(hline,"  0  %3.0d    1  %3.0d %11.4lg %11.4lg %11.4lg %11.4lg %11.4lg\n",
            x_mat->rows, x_mat->rows - 1, sum_regs, sum_regs / (x_mat->rows - 1),
            sum_yws - sum_regs, fcalc, fvalue);
        fputs(hline, fpview);
        fputs(hline, stdout);
        ss_prior = sum_regs;
        }
    cprintf("Input F-value for (1, %d, 1-alpha) for order %d ? ",df , poly_order);
    xcgets(hline, SIZELINE);
    if (hline[0] == NULL)
        break;
    sscanf(hline, "%lf", &fvalue);
    /* calculate F-value for order equal to loop value */
    fcalc = (ss_prior - resids_sum) / resids_sum * df;
    sprintf(hline,"%3.0d  %3.0d  %3.0d  %3.0d %11.4lg %11.4lg %11.4lg %11.4lg %11.4lg\n",
        poly_order, x_mat->rows, poly_order + 1, df, resids_sum, resids_sum / df,
        ss_prior - resids_sum, fcalc, fvalue);
    fputs(hline, fpview);
    fputs(hline, stdout);
    ss_prior = resids_sum;
    }
/* ... ... Analysis of Variance Ends Here ..............................*/
strcpy(xout_file, temp_file);
if(pcpoly == 'y')
    {
    stci_d(ascii, poly_order, 10); /* convert integer order to char */
    strcat(xout_file, ascii);
    }
else
    strcpy(out_root, xout_file);
/* character string for regression data output file */
strcat(xout_file, asc_end);
/* ... ... Regression Data Output To File Begins Here ...................*/
fpname = fopen (xout_file, "w");      /* open file for output */
fprintf (fpname, "%s\n", title);
fprintf (fpname, "%s\n", date);
fprintf (fpname, "Data Points %d,  Parameters %d,  df %d\n\n", x_mat->rows,
    x_mat->cols, df);
fprintf (fpname, "Sums  (x, y, weights)          %11.4lg  %11.4lg  %11.4lg\n",
    sum_x, sum_y, sum_w);
fprintf (fpname, "Weighted Sums  (x, y, xy)      %11.4lg  %11.4lg  %11.4lg\n",
    sum_xw, sum_yw, sum_xyw);
fprintf (fpname, "Weighted Sum of SQ. (x, y)     %11.4lg  %11.4lg\n\n",
    sum_xws, sum_yws);
```

```
    fprintf (fpname, "(Sxx, Syy, Sxy)              %11.4lg  %11.4lg  %11.4lg\n",
       sxx, syy, sxy);
    fprintf (fpname, "(Sy)                                  %11.4lg\n\n", sy);
    fprintf (fpname, "Means  (Xbar, Ybar)          %11.4lg  %11.4lg\n", mean_x, mean_y);
    fprintf (fpname, "Weighted Means (Xbarw, Ybarw) %11.4lg  %11.4lg\n\n", mean_xw, mean_yw);
    fprintf (fpname, "Sums  (y-Yhat, sq(y-Yhat))   %11.4lg  %11.4lg\n",
       resid_sum, resids_sum);
    fprintf (fpname, "Sums  (y-Ybarw, sq(y-Ybarw))  %11.4lg  %11.4lg\n\n",
       sum_reg, sum_regs);
    fprintf (fpname, "Regression Matricies N and G:\n");
    mx_print (*(mat_ptr), fpname);
    mx_print (*(mat_ptr + 1), fpname);
    fprintf (fpname, "\nInverted Regression Matrix:\n");
    mx_print (*(mat_ptr + 2), fpname);
    fprintf (fpname, "\nParameter Matrix:\n");
    mx_print (*(mat_ptr + 3), fpname);
    fprintf (fpname, "\nX-Variable Matrix:\n");
    mx_print (x_mat, fpname);
    fprintf (fpname, "\nY-Variable Matrix:\n");
    mx_print (y_mat, fpname);
    if (err_mat != MXEMPTY && y_mat->rows == err_mat->rows)
       {
       fprintf (fpname, "\nWeighting Matrix:\n");
       mx_print (err_mat, fpname);
       }
    fputc(0x1A, fpname);
    fclose (fpname);            /* close file */
    /* ... ... Regress. Data To File Ends Here ..............................*/
    if(fvalue > fcalc)   /* test to terminate auto-regression */
        {
        break;        /* stop auto-regression */
        }
    /* test that sufficient degrees of freedom exist for auto-regression */
    if(pcpoly == 'y' && poly_order < order_max && (df - 1) > 0)
        {
        mattemp1 = mxc_extract(x_mat, 2, 2);
        /* calculate x variable to power of the next loop order value */
        mattemp2 = mx_pow_elementwise(mattemp1, (double)(poly_order + 1));
        mattemp1 = mx_erase(mattemp1);
        /* attach column containing x values for next order in loop */
        mattemp1 = mxc_cat(x_mat, mattemp2);
        x_mat = mx_erase(x_mat);   /* release memory space from matrix */
        mattemp2 = mx_erase(mattemp2);
        x_mat = mattemp1;
        }
    else
       break;
    }
if(pcpoly == 'y')
    {
    fputc(0x1A, fpview);
    fclose (fpview);        /* close file */
```

```
    }

/* ... Auto-Regression Ends Here ..................................... */

fprintf(stdout,"\n\n");
pause();

for (;;)
    {
    clear_screen();
    cputs("\nREGRESS MENU OPTIONS ARE:\n");
    cputs(" 1  .\n");
    cputs(" 2  RESIDUAL data.\n");
    cputs(" 3  .\n");
    cputs(" 4  .\n");
    cputs(" 5  .\n");
    cputs(" 6  .\n");
    cputs(" 7  PRINT an ASCII file.\n");
    cputs(" 8  PRINT a BINARY file.\n");
    cputs(" 9  RETURN to MAIN menu.\n");
    cputs("\n  Your choice?  ");
    pc = xcgets(hline, SIZELINE);        /* read input */
    cputs("\n");       /* to move cursor to next line */
    switch (*pc)
        {
    case '1':
        break;
    case '2':
        /* ... Residual Section Begins Here ..........................*/
        clear_screen();
        strcpy(view_file, temp_file);
        strcat(view_file, "r");
        strcpy(out_root, view_file);
        strcat(view_file, asc_end);    /* residual file name */
        fpview = fopen(view_file, "w");  /* open file for output */
        fputs(title, fpview);
        fputs("\n", fpview);
        fputs(date, fpview);
        sprintf(hline,"\n\n                    \"TABLE OF RESIDUALS\"\n");
        fputs(hline, fpview);
        fputs(hline, stdout);
        sprintf(hline,"\n\"n_\"  \"Xvalu(1)\"  \"_Weight_\"  \"_Yvalue_\"  \"__Yhat__\"
           \"Residual\"\n\n");
        fputs(hline, fpview);
        fputs(hline, stdout);
        for (i = 0; i < x_mat->rows; i++)
            {
            /* calculate yhat value */
            for (j = 0, yhat = 0; j < x_mat->cols; j++)
                yhat += *(*(matB->element+0)+j) * *(*(x_mat->element+j)+i);
            /* calculate residual value */
            residual = *(*(y_mat->element+0)+i) - yhat;
```

```
            if (err_mat == MXEMPTY || y_mat->rows != err_mat->rows)
               err = 1.0;
            else
               err = *(*(err_mat->element+i)+i);
            sprintf(hline,"%4.0d %11.4lg %11.4lg %11.4lg %11.4lg %11.4lg\n", i+1,
               *(*(x_mat->element+1)+i), err, *(*(y_mat->element+0)+i), yhat, residual);
            fputs(hline, fpview);
            fputs(hline, stdout);
            }
         fprintf(stdout,"\n\n");
         pause();
         fputc(0x1A, fpview);
         fclose(fpview);          /* close file */
         /* ... Residual Section Ends Here ..............................*/
         break;
      case '3':
         break;
      case '4':
         break;
      case '5':
         break;
      case '6':
         break;
      case '7':
         mx_asc_display();
         break;
      case '8':
         mx_bin_display();
         break;
      case '9':
         x_mat = mx_erase(x_mat);   /* release matrix structures in memory */
         y_mat = mx_erase(y_mat);
         err_mat = mx_erase(err_mat);
         for(j = 0; j < 4; ++j)
            *(mat_ptr + j) = mx_erase(*(mat_ptr + j));
         return(0);        /* return to MASTER MENU  */
      default:
         cputs(" Unknown Choice, try again.\n\n");
         break;
         }
      }
   /* end of choose_regress()  */
}

/* ---------------------------------------------------------------------*/
matrix *
mx_regress(x_mat, y_mat, err_mat)
matrix x_mat, y_mat, err_mat;

/* function calculates the N, Q, I, B matrices from X & Y matrices */
{
   matrix matn, matq, matni, matB, mattemp;
```

```
    static matrix mat_array[11];

    if (y_mat->rows != x_mat->rows || y_mat->cols > 1)
        {
        remark("mx_regress: ",  "input matricies do not have correct dimensions");
        return(0);
        }
    if (err_mat == MXEMPTY || y_mat->rows != err_mat->rows)
        mattemp = mx_transpose(x_mat);
    else
        mattemp = mx_multiply(mx_transpose(x_mat), err_mat);

    matn = mx_multiply(mattemp, x_mat);   /* N = X'X or X'VX */
    matq = mx_multiply(mattemp, y_mat);   /* Q = X'Y or X'VY */
    mattemp = mx_erase(mattemp);
    matni = mx_invert(matn);              /* I = (X'X) E-1 */
    matB = mx_multiply(matni, matq);      /* B = IQ

    mat_array[0] = matn;
    mat_array[1] = matq;
    mat_array[2] = matni;
    mat_array[3] = matB;

    return (mat_array);

}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
matrix
get_weight_mat(x_mat)
matrix x_mat;

/* function prepares a weight matrix for mx_regress() */
/* default is err_mat = MXEMPTY */
{
    char hline[SIZEDEC];
    char title[SIZEDEC];
    char date[SIZEDEC];
    char *pc, savepc;
    char err_mat_name[16];
    int  err_row, err_col, j;
    extern int m_rows, m_cols;
    matrix err_mat, err_temp;

    cprintf("Enter WEIGHTING-MATRIX filename (%s is appended), <RETURN> :\n",
    bin_end);
    xcgets(hline, SIZELINE);
    if (hline[0] == NULL)
        err_mat = MXEMPTY;
    else
        {
        strncpy(err_mat_name, hline, 9);
```

```
        strcat(err_mat_name, bin_end);
        cprintf("\nWEIGHTING-MATRIX file is: %s\n\n", err_mat_name);
        err_temp = mx_read(err_mat_name, title, date);
        err_row = m_rows;
        err_col = m_cols;
        cputs("\nIs invertion required to obtain Weighting Matrix. \n");
        cputs("(Y or N) ?   ");
        pc = xcgets (hline, SIZELINE);
        cputs ("\n");
        savepc = tolower(*pc);
        cputs("\nAre Y(i), Y(j) covariance terms included in Error Matrix. \n");
        cputs("(Y or N) ?   ");
        pc = xcgets (hline, SIZELINE);
        tolower(*pc);
        cputs ("\n");
        if (*pc == 'y')
            {
            if (savepc == 'y')
                err_mat = mx_invert(err_temp);  /* complete var & cov matrix provided */
            else
                err_mat = mx_copy(err_temp);  /* complete weight matrix provided */
            }
        else
            {
            err_mat = mx_create(err_row, err_row);
            if (savepc == 'y')
                {
                for (j = 1; j <= err_mat->rows; j++)  /* only variances provided */
                    mx_put_element (err_mat, j, j, (1/mx_get_element (err_temp, j, 1)));
                }
            else
                {
                for (j = 1; j <= err_mat->rows; j++)  /* inverse of var provided */
                    mx_put_element (err_mat, j, j, mx_get_element (err_temp, j, 1));
                }
            }
        err_temp = mx_erase(err_temp);
        }
    .return(err_mat);
}

/* ------------------------------------------------------------------------*/
void
rfc()
/*  Function performs RESPONSE FACTOR CALIBRATION calculations */
/*  The function uses the following four matricies (enter data sequentially into these
*   matricies from data menu choice #2):
*     File      Columns        Rows                Data Type
*     anaXXXX     1      n = # of data points     Analyte Peak Area
*     rsaXXXX     1      n = # of data points     Response Standard Peak Area
*     amwXXXX     1      n = # of data points     Analyte Molecular Weight
*     ancXXXX     1      n = # of data points     Analyte Chlorines/molecule
```

```
*
*   XXXX is the DATA SET CODE
*
*   The function outputs six binary matrices (view with binary print) and
*   one ascii file (view with ascii print):
*
*     File                          Data Type
*     rrxXXXX ..................... Response Ratios
*     lrrXXXX ..................... Log of Response Ratios
*     rfcXXXX ..................... Response Factors
*     acxXXXX ..................... Molar Analyte Chlorine Concentration
*     lacXXXX ..................... Log of Analyte Chlorine Concentration
*     amxXXXX ..................... Analyte Mass Concentration
*     tabXXXX (Ascii File) ........ Summary File of Above Six Matricies
*
*  These output matricies can then be used as input for the multiple regression
*  function.
*/
{
    matrix mat_ana, mat_rsa, mat_amw, mat_anc, mat_rrx, mat_lrr, mat_rfc, mat_acx;
    matrix mat_lac, mat_amx, mat_out, matemp1, matemp2;  /* matrix pointers */

    char hline[SIZEDEC];        /* character string for input */
    char title[SIZEDEC];        /* character string for file title */
    char date[SIZEDEC];         /* character string for date */
    static char file_code[16];  /* character string names to hold file names */
    static char file_ana[16];
    static char file_rsa[16];
    static char file_amw[16];
    static char file_anc[16];
    static char file_rrx[16];
    static char file_lrr[16];
    static char file_rfc[16];
    static char file_acx[16];
    static char file_lac[16];
    static char file_amx[16];
    static char file_tab[16];

    static double rsm, rsmw, rsnc, rscc;   /* double precision variables */

    FILE *fpout;                           /* pointer to output file */

    clear_screen();
    strcpy(file_code, "test");
    cprintf("\nRESPONSE FACTOR CALIBRATION\n\n");
    cprintf("\nEnter Data Set Code (4 Characters)\n"); /* enter data set code */
    xcgets(hline, SIZELINE);
    if(hline[0] != NULL)
        {
        strncpy(file_code, hline, 5);
        }
    strcpy(file_ana, "ana");      /* form input file name strings */
```

```
strcpy(file_rsa, "rsa");
strcpy(file_amw, "amw");
strcpy(file_anc, "anc");
strcpy(file_rrx, "rrx");
strcpy(file_lrr, "lrr");
strcpy(file_rfc, "rfc");
strcpy(file_acx, "acx");
strcpy(file_lac, "lac");
strcpy(file_amx, "amx");
strcpy(file_tab, "tab");
strcat(file_tab, file_code);
strcpy(out_root, file_tab);
strcat(file_tab, asc_end);
strcat(file_code, bin_end);  /* include .mat extention  for file retreval */
cprintf("\nData Set Code is:  %s\n", file_code);
strcat(file_ana, file_code);
strcat(file_rsa, file_code);
strcat(file_amw, file_code);
strcat(file_anc, file_code);
mat_ana = mx_read(file_ana, title, date);   /* READ input data from files */
mat_rsa = mx_read(file_rsa, title, date);
mat_amw = mx_read(file_amw, title, date);
mat_anc = mx_read(file_anc, title, date);

cprintf("\nEnter Response Standard Concentration:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%lf", &rsm);
cprintf("\nEnter Response Standard Molecular Weight:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%lf", &rsmw);
cprintf("\nEnter Number of Chlorines per Molecule for RS:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%lf", &rsnc);
fprintf(stdout, "\n\n");

mat_rrx = mx_div_elementwise(mat_ana, mat_rsa);   /* response ratio */
mat_lrr = mx_log10_elementwise(mat_rrx);        /* log response ratio */
rscc = rsm * rsnc / rsmw;        /* organochlorine concentration for RS */
mat_rfc = mx_mul_scaler((1/rscc), mat_rsa);    /* response factor */
mat_acx = mx_div_elementwise(mat_ana, mat_rfc); /* analyte organochlorine */
mat_lac = mx_log10_elementwise(mat_acx);  /* log analyte organochlorine */
/* analyte mass */
mat_amx = mx_mul_elementwise(mat_acx, mx_div_elementwise(mat_amw, mat_anc));

/* output data to six binary files */
mx_write(mat_rrx, strcat(file_rrx, file_code), mat_rrx->rows, mat_rrx->cols,
    "Response Ratio");
mx_write(mat_lrr, strcat(file_lrr, file_code), mat_lrr->rows, mat_lrr->cols,
    "log(response ratio)");
mx_write(mat_rfc, strcat(file_rfc, file_code), mat_rfc->rows, mat_rfc->cols,
    "Response Factor");
mx_write(mat_acx, strcat(file_acx, file_code), mat_acx->rows, mat_acx->cols,
```

```
        "Analyte Chlorine");
    mx_write(mat_lac, strcat(file_lac, file_code), mat_lac->rows, mat_lac->cols,
        "log(analyte chlorine)");
    mx_write(mat_amx, strcat(file_amx, file_code), mat_amx->rows, mat_amx->cols, "Analyte Mass");

    /* form matrix for summary table  */
    mattemp1 = mxc_cat(mat_rrx, mat_lrr);
    mattemp2 = mxc_cat(mattemp1, mat_rfc);
    mattemp1 = mx_erase(mattemp1);
    mattemp1 = mxc_cat(mattemp2, mat_acx);
    mattemp2 = mx_erase(mattemp2);
    mattemp2 = mxc_cat(mattemp1, mat_lac);
    mattemp1 = mx_erase(mattemp1);
    mat_out = mxc_cat(mattemp2, mat_amx);
    mattemp2 = mx_erase(mattemp2);
    fpout = fopen(file_tab,"w");        /* open ascii file for output */
    fprintf(fpout, "  \"Resp. Ratio\" \"log(RR)\" \"Resp. Factor\" \"Anal. Cl\"  \"log(Cl)\"
        \"Anal. Mass\"\n\n");
    mx_print(mat_out, fpout);    /* output summary information to ascii file */
    fclose(fpout);               /* close ascii file */

    cprintf("Output File Summary:\n");    /* output reminder to console */
    cprintf("rrxCode ..... Response Ratios\n");
    cprintf("lrrCode ..... Log of Response Ratios\n");
    cprintf("rfcCode ..... Response Factors\n");
    cprintf("acxCode ..... Molar Analyte Chlorine Concentration\n");
    cprintf("lacCode ..... Log of Analyte Chlorine Concentration\n");
    cprintf("amxCode ..... Analyte Mass Concentration\n");
    cprintf("tabCode (Ascii File) ..... Summary Table of Above Six Files\n");

    mat_out = mx_erase(mat_out);   /* erase matrix data structures in memory */
    mat_ana = mx_erase(mat_ana);
    mat_rsa = mx_erase(mat_rsa);
    mat_anc = mx_erase(mat_anc);
    mat_amw = mx_erase(mat_amw);
    mat_rrx = mx_erase(mat_rrx);
    mat_lrr = mx_erase(mat_lrr);
    mat_rfc = mx_erase(mat_rfc);
    mat_acx = mx_erase(mat_acx);
    mat_lac = mx_erase(mat_lac);
    mat_amx = mx_erase(mat_amx);

    fprintf(stdout, "\n");
    pause();
    return(0);                  /* return to master menu */
}
/* end of rfc() */

/*-----------------------------------------------------------------*/
void
cen_comp_exp()
/* function for CENTRAL COMPOSITE FACTORIAL EXPERIMENT calculations */
```

```
/*  The function uses a matrix for each factor and the response (enter data
*   sequentially into these matricies from data menu choice #2):
*     File      Columns        Rows                Data Type
*     fac1XXXX    1      n = # of experiments     values for factor #1
*     fac2XXXX    1      n = # of experiments     values for factor #2
*     fac3XXXX    1      n = # of experiments     values for factor #3
*      etc.
*     respXXXX    1      n = # of experiments     values for response
*
*   XXXX is the DATA SET CODE
*
*   The function outputs two binary matrices (view with binary print) and
*   one ascii file (view with ascii print):
*
*     File                          Data Type
*     xxxXXXX ..................... X-matrix for multiple regression
*     yyyXXXX ..................... Y-matrix for multiple regression
*     tabXXXX (Ascii File) ........ Summary File of factors and response
*
*  The xxxXXXX and yyyXXXX output matricies are used as input for the multiple
*  regression function.
*/
{
    matrix mat_1init, mat_2init, mat_1level, mat_2level, mat_input, mat_pow;
    matrix mat_x, mat_y, mat_tab; /*  pointers to matrix structures in memory */
    matrix mat_fac[11];  /* pointer to array of matrix pointers */

    char hline[SIZEDEC];       /* character string for input */
    char title[SIZEDEC];       /* character string for file title */
    char date[SIZEDEC];        /* character string for date */
    static char file_code[16]; /* character string names to hold file names */
    static char file_fac[16];
    static char file_in[16];
    static char file_resp[16];
    static char file_x[16];
    static char file_y[16];
    static char file_tab[16];

    int factor, factor_num, order, order_num, index, row;  /* loop variables */

    char *int_effect;   /*  pointer to character string */
    char ascii[10];     /* character obtained from integer conversion */

    FILE *fpout;         /* file pointer */
    clear_screen();
    strcpy(file_code, "test");
    cprintf("\nCENTRAL COMPOSITE EXPERIMENTAL CALCULATIONS\n\n");
    cprintf("\nEnter Data Set Code (4 Characters)\n"); /* Enter data set code */
    xcgets(hline, SIZELINE);
    if(hline[0] != NULL)
        {
        strncpy(file_code, hline, 5);
```

```
    }
strcpy(file_fac, "fac");          /* form input file name strings */
strcpy(file_resp, "resp");
strcpy(file_x, "xxx");
strcpy(file_y, "yyy");
strcpy(file_tab, "tab");
strcat(file_tab, file_code);
strcpy(out_root, file_tab);
strcat(file_tab, asc_end);
strcat(file_code, bin_end);  /* include .mat extention  for file retreval */
cprintf("\nData Set Code is:  %s\n", file_code);
strcat(file_resp, file_code);
strcat(file_x, file_code);
strcat(file_y, file_code);

cprintf("\nEnter Number of Factors:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%d", &factor_num);
cprintf("\nEnter Number of Experiments:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%d", &row);
cprintf("\nEnter Order of Response Surface Evaluation:  \n");
xcgets(hline, SIZELINE);
sscanf(hline, "%d", &order_num);
if(order_num > 1)
    {
    cputs("\nAre Interaction Effects to be Included in Evaluation. \n");
    cputs("(Y or N) ?   ");
    int_effect = xcgets(hline, SIZELINE);
    fprintf(stdout, "\n\n");
    }
else
    *int_effect = 'n'; /* interaction effects not evaluated if order < 2 */

mat_1init = mx_one(row, 1);    /* input column of ones into X-matrix */
for(factor = 1; factor <= factor_num; factor++) /* loop for all factors */
    {
    strcpy(file_in, file_fac);
    stci_d(ascii, factor, 10);   /* convert integer factor value to char */
    strcat(file_in, ascii);
    strcat(file_in, file_code);
    mat_input = mx_read(file_in, title, date); /* READ input data from files */
    /* include column of factor #? values in X-matrix */
    mat_1level = mxc_cat(mat_1init, mat_input);
    mat_1init = mx_erase(mat_1init);
    mat_2init = mat_1level;
    for(order = 2; order <= order_num; order++) /* loop for all orders of factor */
        {
        mat_pow = mx_pow_elementwise(mat_input, (double)order);
        /* include column of values for factor #? to the ?-order in X-matrix */
        mat_2level = mxc_cat(mat_2init, mat_pow);
        mat_1level = mx_erase(mat_1level);
```

```
        mat_pow = mx_erase(mat_pow);
        mat_2init = mat_2level;
        }
    mat_1init = mat_2init;
    mat_fac[factor-1] = mx_copy(mat_input);  /* save factor #? values */
    mat_input = mx_erase(mat_input);
    }
/* X-matrix includes all orders of all factors at this point, mat_1init */
if(*int_effect == 'y') /* include second order interaction terms if requested */
    {
    for(factor = 1; factor <= factor_num; factor++)
        {
        mat_1level = *(mat_fac + factor - 1);
        for(index = factor + 1; index <= factor_num; index++)
            {
            if(factor != index)
                {
                mat_2level = *(mat_fac + index - 1);
                mat_input = mx_mul_elementwise(mat_1level, mat_2level);
                /* include column of values for factor #? * #?? in X-matrix */
                mat_2init = mxc_cat(mat_1init, mat_input);
                mat_input = mx_erase(mat_input);
                mat_1init = mx_erase(mat_1init);
                mat_1init = mat_2init;
                }
            }
        }
    }
mat_x = mat_1init; /* store completed X-matrix in matrix mat_x */
mat_y = mx_read(file_resp, title, date); /* READ responses into Y-matrix */
/* output X-matrix and Y-matrix to binary files */
mx_write(mat_x, file_x, mat_x->rows, mat_x->cols, "Factorial Experiment -- X matrix");
mx_write(mat_y, file_y, mat_y->rows, mat_y->cols, "Factorial Experiment -- Y matrix");

/* form summary matrix -- includes all factors and response */
mat_1level = *(mat_fac);
factor = 2;
while(factor <= factor_num)
    {
    mat_2level = *(mat_fac + factor - 1);
    mat_tab = mxc_cat(mat_1level, mat_2level);
    mat_1level = mx_erase(mat_1level);
    mat_2level = mx_erase(mat_2level);
    mat_1level = mat_tab;
    factor++;
    }
mat_tab = mxc_cat(mat_1level, mat_y);
mat_1level = mx_erase(mat_1level);
mat_y = mx_erase(mat_y);
mat_x = mx_erase(mat_x);
fpout = fopen(file_tab,"w");  /* open ascii file for output */
fprintf(fpout, "  \"Factors ..... Response\"\n\n");
```

```
    mx_print(mat_tab, fpout);    /* write summary matrix to ascii file */
    fclose(fpout);               /* close ascii file */
    mat_tab = mx_erase(mat_tab); /* erase matrix structures from memory */
    mat_x = mx_erase(mat_x);
    mat_y = mx_erase(mat_y);

    cprintf("Output File Summary:\n");  /* output reminder to console */
    cprintf("xxxCode ..... Factor X Matrix\n");
    cprintf("yyyCode ..... Factor Y Matrix\n");
    cprintf("tabCode ..... Summary Table of Factor and Response Values\n");

    fprintf(stdout, "\n");
    pause();
    return(0);       /* Return to master menu */
}
/*  end of ce_comp_exp() */

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_fdisk()
/*  FILE management menu */
{
    char *pc;     /* pointer into a char string */
    short yy, mm, dd;
    static char erase_name[16], old_name[16], new_name[16];
    char hline[SIZEDEC];

    for (;;)
        {
        clear_screen();
        cputs("\nDISK MANAGEMENT OPTIONS ARE:\n");
        cputs(" 1  LIST disk files.\n");
        cputs(" 2  RENAME disk file.\n");
        cputs(" 3  COPY disk file.\n");
        cputs(" 4  ERASE disk file.\n");
        cputs(" 5  .\n");
        cputs(" 6  PLOT (Changes file to LOTUS 1-2-3 format -- Then use Lotus).\n");
        cputs(" 7  PRINT an ASCII file.\n");
        cputs(" 8  PRINT a BINARY file.\n");
        cputs(" 9  RETURN to MAIN menu.\n");
        cputs("\n  Your choice?  ");
        pc = xcgets(hline, SIZELINE);        /* read input */
        cputs("\n");       /* to move cursor to next line */
        switch (*pc)
            {
        case '1':
            file_list();
            break;
        case '2':
            clear_screen();
            strncpy(old_name," ",16);
            cprintf("Enter DISK:FILENAME to be renamed (%s is not appended), <RETURN> :\n",
```

```
    gen_end);
    xcgets(hline, 16);
    if (hline[0] == NULL)
        break;
    strncpy(old_name, hline,16);
    strncpy(new_name," ",16);
    cprintf("Enter new DISK:FILENAME (%s is not appended), <RETURN> :\n",
    gen_end);
    xcgets(hline, 16);
    if (hline[0] == NULL)
        break;
    strncpy(new_name, hline,16);
    rename(old_name, new_name);
    cprintf("\n%s is renamed to %s !\n\n", old_name, new_name);
    pause();
    break;
case '3':
    clear_screen();
    strncpy(old_name," ",16);
    cprintf("Enter DISK:FILENAME to be copied (%s is not appended), <RETURN> :\n",
    gen_end);
    xcgets(hline, 16);
    if (hline[0] == NULL)
        break;
    strncpy(old_name, hline,16);
    strncpy(new_name," ",16);
    cprintf("Enter new DISK:FILENAME (%s is not appended), <RETURN> :\n",
    gen_end);
    xcgets(hline, 16);
    if (hline[0] == NULL)
        break;
    strncpy(new_name, hline,16);
    fcopy("", old_name, "", new_name);
    cprintf("\n%s is copied to %s !\n\n", old_name, new_name);
    pause();
    break;
case '4':
    clear_screen();
    strncpy(erase_name," ",16);
    cprintf("Enter DISK:FILENAME to be erased (%s is not appended), <RETURN> :\n",
    gen_end);
    xcgets(hline, 16);
    if (hline[0] == NULL)
        break;
    strncpy(erase_name, hline,16);
    unlink(erase_name);
    cprintf("\n%s is erased !\n\n", erase_name);
    pause();
    break;
case '5':
    break;
case '6':
```

```
            mx_2_lotus();
            break;
        case '7':
            mx_asc_display();
            break;
        case '8':
            mx_bin_display();
            break;
        case '9':
            return(0);        /* exit to MAIN menu  */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
    /* end of choose_fdisk()  */
}

/*- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
mx_enter()

/* function enters data into a matrix from keyboard */
{
    matrix mata;
    int i, j, dimc, dimr;
    double value;
    char  hline[SIZEDEC];
    char file_name[16];

    clear_screen();
    strcpy(file_name, prompt_work_file());
    strcpy(out_root, file_name);
    strcat(file_name, bin_end);
    pause();

    clear_screen();
    cputs("\nEnter the number of variables (columns) :  ");
    xcgets(hline, SIZELINE);
    sscanf(hline, "%d", &dimc);

    cputs("\nEnter the number of data points (rows) :  ");
    xcgets(hline, SIZELINE);
    sscanf(hline, "%d", &dimr);

    if(file_name[0] == 'o' && file_name[1] == 'n' && file_name[2] == 'e')
        mata = mx_one(dimr, dimc);
    else
        {
        mata = mx_create(dimr, dimc);

        for (i = 1; i <= dimr; i++)
```

```
            {
            for (j = 1; j <= dimc; j++)
                {
                cprintf("\n Value for row %d  col %d ? ", i, j);
                xcgets(hline, SIZELINE);
                sscanf(hline, "%lf", &value);
                mx_put_element(mata, i, j, value);
                }
            }
        }
    mx_write(mata, file_name, dimr, dimc, comment());
    mata = mx_erase(mata);
    cprintf("\nNew data entries sent to: %s\n\n", file_name);
    pause();
    /* end of mx_enter() */
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_edit()
/*  EDIT menu */
/*  append two matricies */
/*  extract from, replace or delete matrix section */
/*  copy matrix */
{
    char *pc;     /* pointer into a char string */
    int rowtemp, coltemp, num_from, num_to;
    matrix mat_main, mat_sec, mat_out;
    char file_name[16];
    char title[SIZEDEC];
    char date[SIZEDEC];
    char *out_loc;
    char hline[SIZEDEC];
    char xout_file[16];
    char *sec_file;
    extern int m_rows, m_cols;

    mat_main = mat_sec = mat_out = MXEMPTY;  /* show no space allocated */

    strcpy(file_name, file_root);
    strcat(file_name, bin_end);
    for (;;)
        {
        clear_screen();
        cputs("DATA EDIT OPTIONS ARE:\n");
        cputs(" 1  SELECT working data FILENAME.\n");
        cputs(" 2  .\n");
        cputs(" 3  EXTRACT section from data matrix.\n");
        cputs(" 4  APPEND section to data matrix.\n");
        cputs(" 5  REPLACE section of data matrix.\n");
        cputs(" 6  DELETE section of data matrix.\n");
        cputs(" 7  COPY data matrix.\n");
```

```
cputs(" 8  PRINT a BINARY file.\n");
cputs(" 9  RETURN to DATA menu.\n");
cputs("\n  Your choice?  ");
pc = xcgets(hline, SIZELINE);        /* read input */
cputs("\n");       /* to move cursor to next line */
switch (*pc)
    {
case '1':
    mx_main_name();
    strcpy(file_name, file_root);
    strcat(file_name, bin_end);
    break;
case '2':
    break;
case '3':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    cputs("\n'r'ows  '#from'  '#to'.\n");
    cputs("'c'olumns  '#from'  '#to'.\n");
    cputs("\n ?  ");
    pc = xcgets(hline, SIZELINE);
    cputs ("\n");
    switch (tolower(*pc))
        {
    case 'r':
        sscanf(hline, "%*s %d %d", &num_from, &num_to);
        mat_out = mxr_extract (mat_main, num_from, num_to);
        m_rows = num_to - num_from + 1;
        break;
    case 'c':
        sscanf(hline, "%*s %d %d", &num_from, &num_to);
        mat_out = mxc_extract (mat_main, num_from, num_to);
        m_cols = num_to - num_from + 1;
        break;
    default:
        return(0);
        }
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
case '4':
    clear_screen();
    sec_file = prompt_sec_file();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    rowtemp = m_rows;
```

```
        coltemp = m_cols;
        mat_sec = mx_read (sec_file, title, date);
        cputs("\n'r'ows.\n");
        cputs("'c'olumns.\n");
        cputs("\n ?  ");
        pc = xcgets(hline, SIZELINE);
        cputs ("\n");
        switch (tolower(*pc))
            {
        case 'r':
            mat_out = mxr_cat (mat_main, mat_sec);
            m_rows = m_rows + rowtemp;
            m_cols = coltemp;
            break;
        case 'c':
            mat_out = mxc_cat (mat_main, mat_sec);
            m_rows = rowtemp;
            m_cols = m_cols + coltemp;
            break;
        default:
            return(0);
            }
        mat_main = mx_erase(mat_main);
        mat_sec = mx_erase(mat_sec);
        mx_write (mat_out, xout_file, m_rows, m_cols, comment());
        mat_out = mx_erase(mat_out);
        cprintf("\nResulting data sent to: %s\n\n", xout_file);
        pause();
        break;
    case '5':
        clear_screen();
        sec_file = prompt_sec_file();
        strcpy(xout_file, prompt_xout_file());
        strcat(xout_file, bin_end);
        mat_main = mx_read (file_name, title, date);
        rowtemp = m_rows;
        coltemp = m_cols;
        mat_sec = mx_read (sec_file, title, date);
        m_rows = rowtemp;
        m_cols = coltemp;
        cputs("\n'r'ows  '*from'.\n");
        cputs("'c'olumns  '*from'.\n");
        cputs("\n ?  ");
        pc = xcgets(hline, SIZELINE);
        cputs ("\n");
        switch (tolower(*pc))
            {
        case 'r':
            sscanf(hline, "%*s %d", &num_from);
            mat_out = mxr_replace (mat_main, mat_sec, num_from);
            break;
        case 'c':
```

```
        sscanf(hline, "%*s %d", &num_from);
        mat_out = mxc_replace (mat_main, mat_sec, num_from);
        break;
    default:
        return(0);
        }
    mat_main = mx_erase(mat_main);
    mat_sec = mx_erase(mat_sec);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
case '6':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    cputs("\n'r'ows  '#from'  '#to'.\n");
    cputs("'c'olumns  '#from'  '#to'.\n");
    cputs("\n ?  ");
    pc = xcgets (hline);
    cputs ("\n");
    switch (tolower(*pc))
        {
    case 'r':
        sscanf(hline, "%*s %d %d", &num_from, &num_to);
        mat_out = mxr_delete (mat_main, num_from, num_to);
        m_rows = m_rows - (num_to - num_from + 1);
        break;
    case 'c':
        sscanf(hline, "%*s %d %d", &num_from, &num_to);
        mat_out = mxc_delete (mat_main, num_from, num_to);
        m_cols = m_cols - (num_to - num_from + 1);
        break;
    default:
        return(0);
        }
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
case '7':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    mat_out = mx_copy (mat_main);
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
```

```
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '8':
            mx_bin_display();
            break;
        case '9':
            return(0);        /* exit to DATA MENU */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
    /* end of choose_edit()  */
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_transform()
/*  TRANSFORMATION menu */
/*  use scalars or functions to transform data in a matrix */
{
    char *pc;     /* pointer into a char string */
    matrix mat_main, mat_out;
    double amount;
    char file_name[16];
    char title[SIZEDEC];
    char date[30];
    char *out_loc;
    char hline[SIZEDEC];
    char xout_file[16];
    char *sec_file;
    extern int m_rows, m_cols;

    mat_main = mat_out = MXEMPTY;  /* show no space allocated */

    strcpy(file_name, file_root);
    strcat(file_name, bin_end);
    for (;;)
        {
        clear_screen();
        cputs("SCALAR AND FUNCTION OPERATIONS ARE:\n");
        cputs(" 1  SELECT working data FILENAME.\n");
        cputs(" 2  SCALAR ADDITION to data matrix.\n");
        cputs(" 3  SCALAR MULTIPLY to data matrix.\n");
        cputs(" 4  LOGARITHM of data matrix elements.\n");
        cputs(" 5  POWER, SQUARE ROOT or INVERSE of data matrix elements.\n");
        cputs(" 6  EXPONENTIAL of data matrix elements.\n");
        cputs(" 7  TRIGONOMETRIC of data matrix elements.\n");
        cputs(" 8  PRINT a BINARY file.\n");
        cputs(" 9  RETURN to EDIT menu.\n");
```

```
cputs("\n  Your choice?  ");
pc = xcgets(hline, SIZELINE);        /* read input */
cputs("\n");       /* to move cursor to next line */
switch (*pc)
    {
case '1':
    mx_main_name();
    strcpy(file_name, file_root);
    strcat(file_name, bin_end);
    break;
case '2':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    cputs ("\n Enter scalar value :  ");
    xcgets (hline, SIZELINE);
    sscanf (hline, "%lf", &amount);
    mat_out = mx_add_scalar (amount, mat_main);
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
case '3':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    cputs ("\n Enter scalar value :  ");
    xcgets (hline, SIZELINE);
    sscanf (hline, "%lf", &amount);
    mat_out = mx_mul_scalar (amount, mat_main);
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
case '4':
    clear_screen();
    strcpy(xout_file, prompt_xout_file());
    strcat(xout_file, bin_end);
    mat_main = mx_read (file_name, title, date);
    mat_out = mx_log_choose (mat_main);
    mat_main = mx_erase(mat_main);
    mx_write (mat_out, xout_file, m_rows, m_cols, comment());
    mat_out = mx_erase(mat_out);
    cprintf("\nResulting data sent to: %s\n\n", xout_file);
    pause();
    break;
```

```
        case '5':
            clear_screen();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            mat_out = mx_pow_choose (mat_main);
            mat_main = mx_erase(mat_main);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '6':
            clear_screen();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            mat_out = mx_exp_choose (mat_main);
            mat_main = mx_erase(mat_main);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '7':
            clear_screen();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            mat_out = mx_trig (mat_main);
            mat_main = mx_erase(mat_main);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '8':
            mx_bin_display();
            break;
        case '9':
            return(0);        /* exit to DATA MENU */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
    /* end of choose_transform()  */
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
void
choose_matrix_op()
```

```
/*  MATRIX OPERATIONS menu */
/*  perform elementwise or matrix operations for two matrices */
/*  transpose or invert a single matrix */
{
    char *pc;     /* pointer into a char string */
    int rowtemp;
    matrix mat_main, mat_sec, mat_out;
    double amount;
    char file_name[16];
    char title[SIZEDEC];
    char date[SIZEDEC];
    char *out_loc;
    char hline[SIZEDEC];
    char xout_file[16];
    char *sec_file;
    extern int m_rows, m_cols;

    mat_main = mat_sec = mat_out = MXEMPTY;  /* show no space allocated */


    strcpy(file_name, file_root);
    strcat(file_name, bin_end);
    for (;;)
        {
        clear_screen();
        cputs("ELEMENTWISE AND MATRIX OPERATIONS ARE:\n");
        cputs(" 1  SELECT working data FILENAME.\n");
        cputs(" 2  ADD two data matricies ELEMENTWISE.\n");
        cputs(" 3  SUBTRACT two data matricies ELEMENTWISE.\n");
        cputs(" 4  MULTIPLY two data matricies ELEMENTWISE.\n");
        cputs(" 5  DIVIDE two data matricies ELEMENTWISE.\n");
        cputs(" 6  MATRIX MULTIPLY two data matricies.\n");
        cputs(" 7  TRANSPOSE data matrix.\n");
        cputs(" 8  INVERT data matrix.\n");
        cputs(" 9  RETURN to DATA menu.\n");
        cputs("\n  Your choice?  ");
        pc = xcgets(hline, SIZELINE);        /* read input */
        cputs("\n");       /* to move cursor to next line */
        switch (*pc)
            {
        case '1':
            mx_main_name();
            strcpy(file_name, file_root);
            strcat(file_name, bin_end);
            break;
        case '2':
            clear_screen();
            sec_file = prompt_sec_file();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_sec = mx_read (sec_file, title, date);
            mat_main = mx_read (file_name, title, date);
```

```
        mat_out = mx_add (mat_main, mat_sec);
        mat_main = mx_erase(mat_main);
        mat_sec = mx_erase(mat_sec);
        mx_write (mat_out, xout_file, m_rows, m_cols, comment());
        mat_out = mx_erase(mat_out);
        cprintf("\nResulting data sent to: %s\n\n", xout_file);
        pause();
        break;
    case '3':
        clear_screen();
        sec_file = prompt_sec_file();
        strcpy(xout_file, prompt_xout_file());
        strcat(xout_file, bin_end);
        mat_sec = mx_read (sec_file, title, date);
        mat_main = mx_read (file_name, title, date);
        mat_out = mx_subtract (mat_main, mat_sec);
        mat_main = mx_erase(mat_main);
        mat_sec = mx_erase(mat_sec);
        mx_write (mat_out, xout_file, m_rows, m_cols, comment());
        mat_out = mx_erase(mat_out);
        cprintf("\nResulting data sent to: %s\n\n", xout_file);
        pause();
        break;
    case '4':
        clear_screen();
        sec_file = prompt_sec_file();
        strcpy(xout_file, prompt_xout_file());
        strcat(xout_file, bin_end);
        mat_sec = mx_read (sec_file, title, date);
        mat_main = mx_read (file_name, title, date);
        mat_out = mx_mul_elementwise (mat_main, mat_sec);
        mat_main = mx_erase(mat_main);
        mat_sec = mx_erase(mat_sec);
        mx_write (mat_out, xout_file, m_rows, m_cols, comment());
        mat_out = mx_erase(mat_out);
        cprintf("\nResulting data sent to: %s\n\n", xout_file);
        pause();
        break;
    case '5':
        clear_screen();
        sec_file = prompt_sec_file();
        strcpy(xout_file, prompt_xout_file());
        strcat(xout_file, bin_end);
        mat_sec = mx_read (sec_file, title, date);
        mat_main = mx_read (file_name, title, date);
        mat_out = mx_div_elementwise (mat_main, mat_sec);
        mat_main = mx_erase(mat_main);
        mat_sec = mx_erase(mat_sec);
        mx_write (mat_out, xout_file, m_rows, m_cols, comment());
        mat_out = mx_erase(mat_out);
        cprintf("\nResulting data sent to: %s\n\n", xout_file);
        pause();
```

```
            break;
        case '6':
            clear_screen();
            sec_file = prompt_sec_file();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            rowtemp = m_rows;
            mat_sec = mx_read (sec_file, title, date);
            mat_out = mx_multiply (mat_main, mat_sec);
            m_rows = rowtemp;
            mat_main = mx_erase(mat_main);
            mat_sec = mx_erase(mat_sec);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '7':
            clear_screen();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            mat_out = mx_transpose (mat_main);
            mat_main = mx_erase(mat_main);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '8':
            clear_screen();
            strcpy(xout_file, prompt_xout_file());
            strcat(xout_file, bin_end);
            mat_main = mx_read (file_name, title, date);
            mat_out = mx_invert (mat_main);
            mat_main = mx_erase(mat_main);
            mx_write (mat_out, xout_file, m_rows, m_cols, comment());
            mat_out = mx_erase(mat_out);
            cprintf("\nResulting data sent to: %s\n\n", xout_file);
            pause();
            break;
        case '9':
            return(0);        /* exit to DATA MENU */
        default:
            cputs(" Unknown Choice, try again.\n\n");
            break;
            }
        }
    /* end of choose_matrix_op()  */
}
```

```
/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
#include <math.h>
matrix
mx_create(no_rows, no_cols)
    int no_rows, no_cols;
/* create and allocate memory for a matrix structure */
{
    matrix mat;

    if((mat = mx_alloc_struct(no_rows, no_cols)) != MXEMPTY)
        {
        if(mx_mem_alloc(mat) == MXEMPTY)
            {
            free(mat->element);
            free(mat);
            mat = MXEMPTY;
            }
        }
    return(mat);
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
#include <math.h>
matrix
mx_alloc_struct(no_rows, no_cols)
    int no_rows, no_cols;
/* allocate memory for the matrix structure and column pointer array */
{
    matrix mat;

    if ((mat = (matrix) calloc(1, sizeof(mx_mtx))) != MXEMPTY)
        {
        mat->rows = no_rows;
        mat->cols = no_cols;
        mat->element = (double **) calloc(mat->cols,sizeof(mat->element));

        if (mat->element == MXEMPTY)
            {
            free(mat);
            mat = (matrix) MXEMPTY;
            }
        }
    if (mat == MXEMPTY)
        fatal("mx_alloc_struct: ", "Can't allocate matrix.");

    return(mat);
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
#include <math.h>
int
mx_mem_alloc(mat)
```

```
    matrix mat;
/* allocate memory space for matrix elements */
{
    int i, j, returncode = OKCODE;

    if(mat != MXEMPTY && mat->rows > 0 && mat->cols > 0)
          /* need brackets here to force else to associate with this if */
        {
        for(i = 0; i < mat->cols; i++)
            {
            if((*(mat->element + i) =
                  (double *) calloc(mat->rows, sizeof(double))) == MXEMPTY)
                {
                returncode = MXEMPTY;
                for(j = 0; j < i; j++)
                  /* free already allocated memory */
                free(*(mat->element + j));
                break;
                }
            }
        }
    else
        returncode = MXEMPTY;

    if(returncode == MXEMPTY)
        fatal("mx_mem_alloc: ","Can't allocate memory.");

    return(returncode);
}

/*------ - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - */
#include <math.h>
matrix
mx_erase(mat)
    matrix mat;
/* release assigned memory space used for a matrix */
{
    int i;    /* loop variable */

    if (mat != MXEMPTY )
        {
        for (i = 0; i < mat->cols; i++)
            {
            free(*(mat->element + i));
            }
        free(mat->element);
        free(mat);
        }
    mat = (matrix) MXEMPTY;   /*  show no space allocated */
    return(mat);
}
```

Appendix E

List of Related Projects Not Reported in This Thesis

1. Separation and purification of polychlorinated butadienes and butenes by HPLC.

2. Identification of impurities present in purchased polychlorinated butadiene and butene mixtures by mass spectrometry.

3. Measurements of chlorophenols, hexachlorobenzene, DDE, heptachlor, and toxaphene with the GC-HECD.

Appendix F

Copyright Release from the Journal of Chromatography

ELSEVIER
SCIENCE
PUBLISHERS
Science & Technology Division

Postal address:
P.O. Box 330
1000 AH Amsterdam
The Netherlands
Telephone (020) 5803 911
Telephone ext. (020) 5803355
Telex 18582 ESPA NL
Cables Elapubco

Address for visitors:
Molenwerf 1
Amsterdam, The Netherlands

Mr. T.L. Ramus
Oregon State University
Department of Chemistry
Corvallis, OR 97331
U.S.A.

Our ref. RM/cb Your ref. Amsterdam, May 13, 1985

Agriculture
Chemistry
Earth Sciences
Social Sciences
Technology & Engineering
Dictionaries

Affiliated Company:
Applied Science Publishers
Barking (U.K.)

Re: "Determinations of Chlorinated Hydrocarbons by Gas Chromatography Using Response Factor Calibration" J. Chromatogr., 314 (1984) 243-251.

"Temperature Selection of Chlorinated Hydrocarbon Reduction for the Hall Electrolytic Conductivity Detector" J. Chromatogr. 328 (1985) 342-346.

Dear Mr. Ramus,

Thank you for your letter of April 17, 1985.

It is with pleasure that we grant you permission to reproduce the articles originally appearing in the above-mentioned publications in their entirety in your doctoral thesis. This permission is given with the understanding that it applies only to your thesis and that full acknowledgement is given to their sources.

We wish you much success with your future work.

Yours sincerely,
ELSEVIER SCIENCE PUBLISHERS

Robert J. Marx