

SPECTROGRAPHIC ANALYSIS FOR SILVER OF
RAINWATER FROM CLOUD SEEDING

by

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SPECTROGRAPHIC ANALYSIS FOR SILVER OF RAINWATER FROM CLOUD SEEDING

INTRODUCTION

During the past three years, a program to evaluate attempts to increase precipitation by silver iodide cloud seeding in an area consisting of Gilliam, Morrow and Sherman counties of north-central Oregon has been conducted by the Oregon Agricultural Experiment Station. A particular phase of this evaluation program required the analysis of a series of rainwater samples for possible traces of silver due to the silver iodide seeding agent. During the six weeks period from February 19 to March 1, 1951, weekly precipitation samples were collected at twenty different stations in the Northwest (2, p.21), and submitted to the Physics Department of Oregon State College for spectrographic analysis. Sample collection was made by various federal, state and private agencies in cooperation with the Oregon Agricultural Experiment Station. For a complete list of cooperating agencies and personnel and a list of the collecting stations, the reader is referred to the acknowledgment page and Table V of the appendix of Beaumont (2).

This paper describes in detail the development of the spectrographic method employed for analysis, the equipment used and the application of the method to the unknown

samples. In addition, the method is summarized in the form of a detailed procedure for analyses in the hope that it might serve as a useful guide for future analyses of this type.

No attempt is made in this paper to evaluate the results of the analyses as to the effectiveness of cloud seeding in increasing natural precipitation. For this information, as well as a detailed discussion of the entire evaluation program, the reader is referred to "Four Years of Cloud-Seeding in Tri-Counties, Oregon" to be published by the Oregon Agricultural Experiment Station upon the completion of their evaluation project.

EQUIPMENT

Spectrograph

The spectrograph employed in this investigation is a Jarrell-Ash Company, Wadsworth mounting, concave grating spectrograph. The four inch diameter aluminum on glass grating has a radius of curvature of 4.8 meters and a ruling of 15,000 lines/inch. The spectrograph has a guaranteed resolution of 0.07 at 3,000 Angstroms and a linear dispersion of 7 Angstroms/mm in the first order spectrum. Its speed in terms of its relative aperture is $f/23.6$. The combination of high resolution and high dispersion, and the anastigmatic characteristics of the normal Wadsworth type mounting, makes this instrument especially useful for spectrochemical applications of the type herein described.

Power Source

The power source used in this work is a National Spectrographic Laboratory "Spec Power". This supply features three standard type excitation units, providing power for a low voltage direct current arc, an alternating current arc, and a radio frequency high voltage spark. The source is provided with an oscilloscope and appropriate ammeters for the arc and spark currents, so that excitation conditions may be noted throughout the arcing cycle and appropriate adjustments made immediately, if necessary.

The time duration of the arcing cycle is controlled by pre-exposure and total exposure timers which are incorporated in the unit. These timers control the exposure of the photographic plate by actuating an electromagnetically operated shutter located behind the spectrograph slit.

The alternating current arc is used as the mode of excitation throughout this project. This unit of the power source is supplied with a 10 KVA transformer which delivers up to 4.2 amperes at 2400 volts (RMS) or 2 amperes at 4800 volts (RMS). The current may be controlled easily by varying the primary inductance. The 4800 volt discharge is self-igniting, while the 2400 volt discharge is initiated by an auxiliary spark unit which applies a high potential, high frequency voltage of low energy across the electrode gap. Once the discharge has been initiated, the high voltage is removed and the discharge maintained by the alternating current supply. The auxiliary spark unit was designed and constructed by Dr. Duis Bolinger and utilizes a modified form of the circuit first suggested by Brockman and Hochgesang (14, p.746).

Microphotometer

A Jarrell-Ash Company projection comparator microphotometer is used to determine the blackness of spectrum lines used for quantitative determinations in this work.

Enlarged images of a master spectrogram and a spectrogram upon which measurements are to be made are projected adjacent to one another upon a viewing screen. Positive identification of spectrum lines is readily accomplished by comparison with the master plate. The blackness of a particular line is determined by moving its image laterally across a uniformly illuminated slit in the viewing screen. A barrier layer photovoltaic cell, whose terminals are connected to a sensitive galvanometer, is located beneath the viewing screen. The characteristics of the galvanometer-photocell circuit are such that the galvanometer deflection is a linear function of the illumination of the photocell. The per cent transmission of a spectrum line being measured is indicated directly on the galvanometer deflection scale.

The apparatus described briefly above constitutes the major equipment available and currently in use in the Spectrograph Laboratory of the Physics Department at Oregon State College. For further information concerning the above apparatus the reader is referred to the literature provided by the manufacturer. Other minor equipment, pertinent to this particular investigation, is described in detail in the section on development of the analytical method.

DEVELOPMENT OF THE ANALYTICAL METHOD

Introduction

The present analytical problem involves basically the application of optical spectrographic emission procedures to the analysis of rainwater for traces of silver. As mentioned earlier, the silver is presumed to be due to the silver iodide seeding agent. Since silver iodide is soluble in water only to the extent of 3×10^{-6} grams per 100 milliliters of hot water, it is expected that the samples will consist of silver in very dilute solution and possible small amounts of silver iodide present as solid matter.

The application of spectrographic methods to problems involving metallic impurities in solution is not new. In the past, numerous investigators have developed and described procedures for the analysis of solutions based on the emission spectra produced by excitation of the liquid sample or its residue (7, pp.410-413), (8, pp.24-27), (9, pp.10-15), and (15 pp.260-261). The application of these and other techniques has been widespread, and today various spectrographic methods are successfully applied to a wide variety of soluble materials such as metallic impurities in plating-bath electrolytes, inorganic and pharmaceutical chemicals, beverages, volatile liquors, sea and mineral water, and blood and other body fluids, as well as

numerous others (14, pp.283-284).

The various procedures which are used for these and other analyses differ primarily in the manner in which the sample is excited. In the present method the liquid sample is deposited and evaporated on graphite electrodes and the residue excited by means of a high voltage alternating current arc discharge between the electrodes. This method was first suggested by Duffendack and Thompson (6, pp.304-305) and later applied to the analysis of caustic liquors for very small concentrations of metallic traces by Duffendack and Wolfe (8, pp.24-27). The method is characterized by extremely high sensitivity and moderate precision. For a discussion of the characteristics and applicability of other modes of sample excitation such as direct current arcs, high frequency spark, acetylene flames, and others, the reader is referred to Nachtrieb (14, pp.190-202) or Brode (4, pp.44-58).

Choice of Internal Standards

The method used in this work is based on the well known and widely used internal standard principle first suggested by Gerlach (10, pp.383-400). This principle involves the addition of a fixed concentration of some element, not originally present in the unknown samples, to both standard and unknown samples alike. Care is exercised, not only in the selection of the standard

element, but also in the selection of the analysis and standard lines in order that fluctuations in the excitation and photographic processes will affect the intensities of the analysis and standard lines in an identical manner. Under these conditions, the intensity ratio of the analysis and internal standard lines is not affected appreciably by unavoidable factors of variation and depends only upon the concentration of the analysis element.

Ahrens (1, pp.81-83) discusses in detail the factors which should be considered when choosing an internal standard. The major factors are: the internal standard should be an element which is not contained in any appreciable amount in the unknown samples, it should have a volatilization rate quite similar to that of the analysis element, and it should be available in a high state of purity with respect to the analysis element; the internal standard and analysis lines should have similar excitation potentials and roughly the same wavelength, so as to reduce errors due to the photographic measurement of radiant energy; and the internal standard line should be free from self-absorption. While it may, in some instances, be possible to choose a proper internal standard by consideration of the above factors alone, it is perhaps more practical to let them serve as a guide in choosing a group of elements as probable standards, and make the final selection from this group by consideration of data obtained under actual burning condi-

tions. This procedure was followed in the determination of the internal standard used in this work.

On the basis of the above factors, gallium, germanium, molybdenum, and tin were selected as likely standards; copper and gold, which at first appeared to be suitable, were rejected because of the presence of copper in the unknown samples and the lack of gold in a convenient form. Tin was ultimately chosen as the internal standard from this group. The final choice was made on the basis of data obtained from a time-study or, as it is often called, a moving plate spectrogram. Test samples, containing both the internal standard and analysis elements, are prepared and arced for three or four minutes. At equal time intervals, say every 20 or 30 seconds (the length of the time interval depends on the sensitivity of the elements concerned as well as the relative amount present), the photographic plate is rapidly moved parallel to the spectrograph slit a distance equal to the length of the slit. The spectrogram obtained in this manner provides an actual history of the behavior of the analysis and proposed internal standard elements under identical conditions. The data is conveniently represented by a plot of logarithm of the intensity ratios of analysis and internal standard lines for successive time intervals versus total arcing time.

Fig. 1 shows such a plot for the elements under consideration as standards for this method. It may be seen

from this plot, that the ratio $\frac{I_{Ag\ 3280.7}}{I_{Ge\ 3269.5}}$ increases continually with time, while the ratio $\frac{I_{Ag\ 3280.7}}{I_{Mo\ 3170.3}}$ remains fairly constant but fluctuates rather widely from the mean. The ratios $\frac{I_{Ag\ 3280.7}}{I_{Sn\ 3262.3}}$ and $\frac{I_{Ag\ 3280.7}}{I_{Ga\ 2943.6}}$, however, are nearly constant, while the fluctuations are relatively small. From this data, both tin and gallium appear to be suitable as internal standards for silver. Tin was finally selected because it was readily available in a convenient form in a high state of purity with respect to silver.

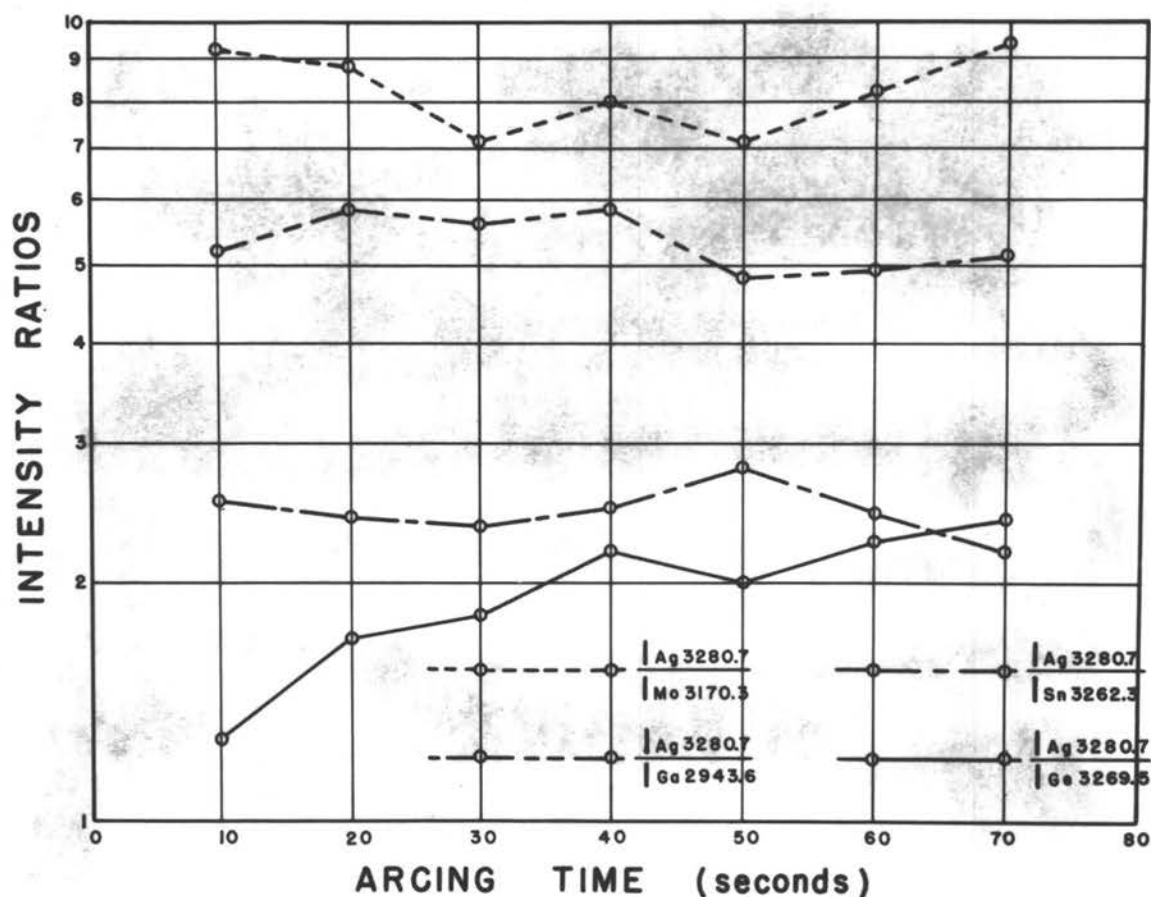


Fig. 1 Time Study

Preparation of Standard Solutions

Before proceeding further with the development of the method, it is desirable to prepare the standard silver solutions upon which the determination of the silver content in unknown samples will ultimately be based. However, it is necessary first to determine the approximate range of concentrations expected in the rainwater samples so that standard solutions of appropriate concentrations may be prepared.

An attempt was made to determine the order of magnitude of the expected silver content in unknown samples by calculating the amount of silver iodide in a given volume of rainwater, based on the assumption that the rainwater resulted from the nucleation of a supercooled cloud by silver iodide. Vonnegut (18, p.282) has demonstrated that silver iodide particles of the order of 100 Angstroms in diameter are effective as nuclei for the formation of ice crystals in a supercooled cloud. These ice crystals might then be expected to grow in size at the expense of the supercooled water droplets in the cloud. If we assume that a raindrop is formed by the melting of a snowflake which originated as an ice crystal on a silver iodide particle, then the concentration of silver iodide in the raindrop is given by

$$C = (\rho_s V_s) / (\rho_s V_s + \rho_w V_w) \quad (1)$$

where C is the concentration of silver iodide, ρ_s the density of silver iodide, V_s the volume of the silver iodide particle, ρ_w the density of water, and V_w the volume of the raindrop. Taking the radius of the average raindrop to be 0.1 cm and the radius of the average silver iodide particle to be 50 Angstroms and assuming the volume of each to be equivalent to the volume of a sphere of corresponding radius, we obtain for the approximate concentration

$$C = \rho_s R_s^3 / \rho_w R_w^3 \quad (2)$$

$$C = \frac{(5.72 \text{ gm/cm}^3)(50 \times 10^{-8} \text{ cm})^3}{(1 \text{ gm/cm}^3)(0.1 \text{ cm})^3}$$

$$C = 7.2 \times 10^{-16} \approx 10^{-15}$$

The author knows of no method, spectrographic or other, that even remotely approaches the sensitivity required for the detection of such minute traces. However, a preliminary analysis of representative samples indicated silver in concentrations estimated to be as high as a few parts per million in some samples. The question immediately arose as to the source of these surprisingly large amounts of silver. Extensive blanks, which were processed along with the test samples, indicated no contamination due to preliminary preparation of samples. It was concluded, therefore, that

the silver present in excess of the amount predicted by the above calculation was due to any or all of the following:

(1) contamination of the samples resulting from improperly cleaned containers and/or from foreign matter introduced during collection; (2) direct fall-out of the silver iodide particles accompanied with or without precipitation; (3) silver as a contaminant in the atmosphere. It is also quite possible that the calculated value of the expected concentration is too low. It is realized that a raindrop stands a good chance of colliding with other silver iodide nuclei as it falls from the cloud base to the earth. This would, of course, increase the silver iodide concentration of the raindrop by a factor equal, approximately, to the number of additional nuclei acquired. However, it is extremely doubtful that this effect could account for the very great discrepancy between the computed and experimental values.

The results of the calculation and preliminary analyses, mentioned in the preceding paragraph, indicated that the rainwater samples might contain silver in concentrations ranging from 10 parts per million down to undetectable amounts. To adequately cover this concentration range, a series of ten standard silver solutions, ranging in concentration from 0.001 to 316 parts per million were prepared. In establishing any spectrographic method for the analysis of unknown samples, it is desirable that the

standard samples approximate the composition of the unknowns insofar as possible. For reasons discussed in detail in a later section, the rainwater samples were evaporated to dryness and a solution of acetone and potassium iodide added to the residue. The standard solutions were prepared accordingly, using a solution of acetone and potassium iodide as the solvent for the silver iodide. A stock solution, containing one part per million of tin by weight is first prepared by adding a weighed amount of stannous chloride to a measured volume of acetone, containing 0.2 milligrams of potassium iodide per milliliter of solution. Weighed amounts of silver iodide are then added to measured volumes of this stock solution so as to obtain two standard solutions containing 100 and 316 parts per million silver by weight. By successive dilutions of these solutions with the stock solution, standard solutions of 31.6, 10, 3.16, 1, 0.316, 0.1, 0.0316, 0.01, and 0.001 parts per million silver are obtained.

Stringent precautions are necessary to minimize contamination of the standard solutions. Blanks are run on all the reagents used; the stannous chloride must be pure with respect to silver and the silver iodide with respect to tin, while the acetone and potassium iodide cannot contain either silver or tin. The glassware used for the preparation and storage of standard solutions is cleaned with detergent and hot water, rinsed several times in hot

water, rinsed with a solution of potassium dichromate and sulfuric acid followed by several hot water rinses, rinsed with aqua-regia followed by several distilled water rinses, and finally thoroughly steamed.

The standard solutions are stored in pyrex flasks, and, although probable contamination through leeching of impurities from the glass was anticipated, this did not prove bothersome as far as silver and tin were concerned. The possibility of loss in titer due to absorption, discussed by Leutwein (13, pp.129-133), should be kept in mind when storing the standard solutions for any appreciable period. The solutions are kept in tightly stoppered bottles in a cool, dark place and they remain quite stable under these storage conditions.

Preparation of Electrodes

Flat-topped graphite rods, $1/4$ inch in diameter and $1/2$ inch in length, are used as both upper and lower electrodes. These electrodes are made from National Carbon Company special-purity 12 inch graphite rods and are formed by cutting the rods to length by means of a small abrasive saw of the type used by jewelers. Fig. 2 shows a photograph of the electrode cutting assembly consisting of the abrasive saw mounted on the shaft of a small electric motor and a simple hardwood vise to hold the graphite rod during cutting. The electrode guide is made by boring a $1/4$ inch

hole through the vise as indicated in the figure. The vise is hinged to its base in such a manner that a slight rotation about the connecting pin will result in the movement of the graphite rod into the saw and thus accomplish the cutting process. In order to insure a good square cut, the relative positions of the motor and the vise are such that the graphite rod is always held parallel to the motor shaft.

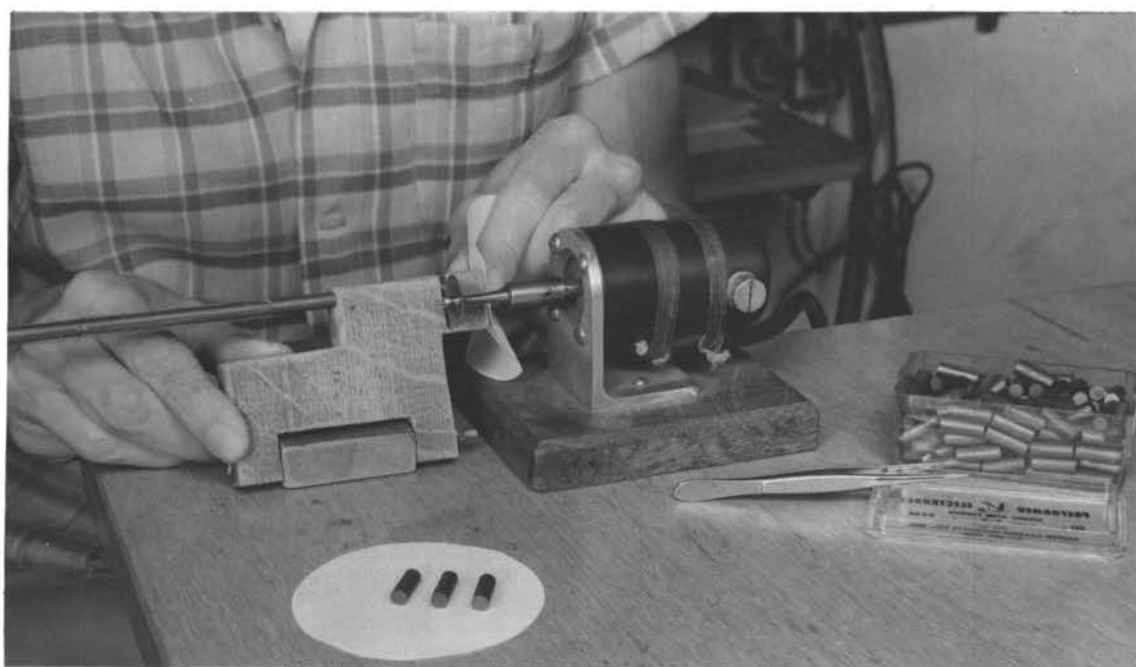


Fig. 2 Electrode Cutter

With the aid of this device, two or three hundred good electrodes may be cut in one hour. The surface of the electrodes cut in this manner is extremely smooth and square. Tests showed no contamination with regard to silver and tin resulting from the use of either the abrasive saw or the hardwood guide. The electrodes are always handled with

forceps or clean filter paper during and after forming and are stored in dust-tight containers prior to using.

Evaporation of Samples on Electrodes

The deposition of samples on the electrodes is accomplished by the evaporation of the standard solutions directly from the tips of the upper and lower electrodes before arcing. Both electrodes are used as it was found to be easier to deposit a given amount of solution between the two than all on one. There is no preference between upper and lower electrodes in the alternating current arc. The solutions are deposited dropwise by means of loc capacity Becton-Dickensen tuberculin type syringes, and allowed to evaporate to dryness at room temperature. While it is not necessary to determine accurately the amount of solution dispensed on each electrode, it is desirable to keep the amount above predetermined limits in order to insure the presence of a detectable amount of residue on each electrode. Several electrode pairs (upper and lower) are prepared for standard concentration, so that several determinations of the intensity ratio of silver to tin lines may be made for each concentration. In order to conserve time when preparing several electrodes for a given concentration, the liquid is deposited dropwise to each one in rotation until approximately one cubic centimeter of solution has been deposited on each. In this manner, a dozen or so

electrodes for a single concentration may be prepared in approximately thirty minutes. The preparation of an equal number of electrodes for different concentrations is, of course, more time consuming.

Ahrens (1, pp.77-78), Brode (4, p.49), Harvey (12, p.345), and others have suggested that the tips of graphite electrodes be coated with a material impervious to the solution being evaporated in order to minimize absorption by the graphite and thus attain increased sensitivity due to the fact that most of the residue is deposited on the top of the electrodes where it may be readily excited. Collodion, paraffin, and kerosene have been suggested as probable coatings. However, none of these proved satisfactory for the acetone solutions used here; the collodion was dissolved by the acetone and hence rendered useless, the presence of the paraffin prevented complete drying of the sample, while kerosene appeared to have little or no effect on the rather appreciable absorption of the acetone solution by the graphite. A number of other likely materials including various commercial resins and greases were tested. A silicone lubricant called "high vacuum grease", produced by Dow Chemical Corporation, proved to be excellent for these purposes. A very thin layer of this grease, applied to the electrode tips with a clean wood paddle, gives a surface quite impervious to acetone. This grease was found to be free of silver and tin and its

spectrum is quite simple, producing no interference with the silver and tin lines used. The sensitivity of the method was increased by a factor of four or five by the use of this coating.

It is desirable to burn the electrodes as soon after preparation as possible. While precision is not adversely affected by the storage of electrodes in a dust free, dry place for a day or two, extended storage may cause erratic results due to contamination and moisture acquired during this period. When circumstances made it impossible to excite the electrodes immediately after preparation, they were stored in tightly sealed plastic containers. Immediately prior to burning, all electrodes were preheated to a temperature of approximately 90 degrees Centigrade and allowed to remain at this temperature for a matter of ten minutes or so. It was felt that any variations in excitation resulting from dampness in the electrode material might be nullified by this procedure. The preheating was done in the electrode heater shown in Fig. 3. This device is used primarily to supply heat to electrodes in order to speed up the evaporation of non-volatile liquid samples. Although it was not used in this capacity in this particular work, it is perhaps of general interest to those working in the field of spectrographic analysis as applied to solutions. Accordingly, a brief description is given below.

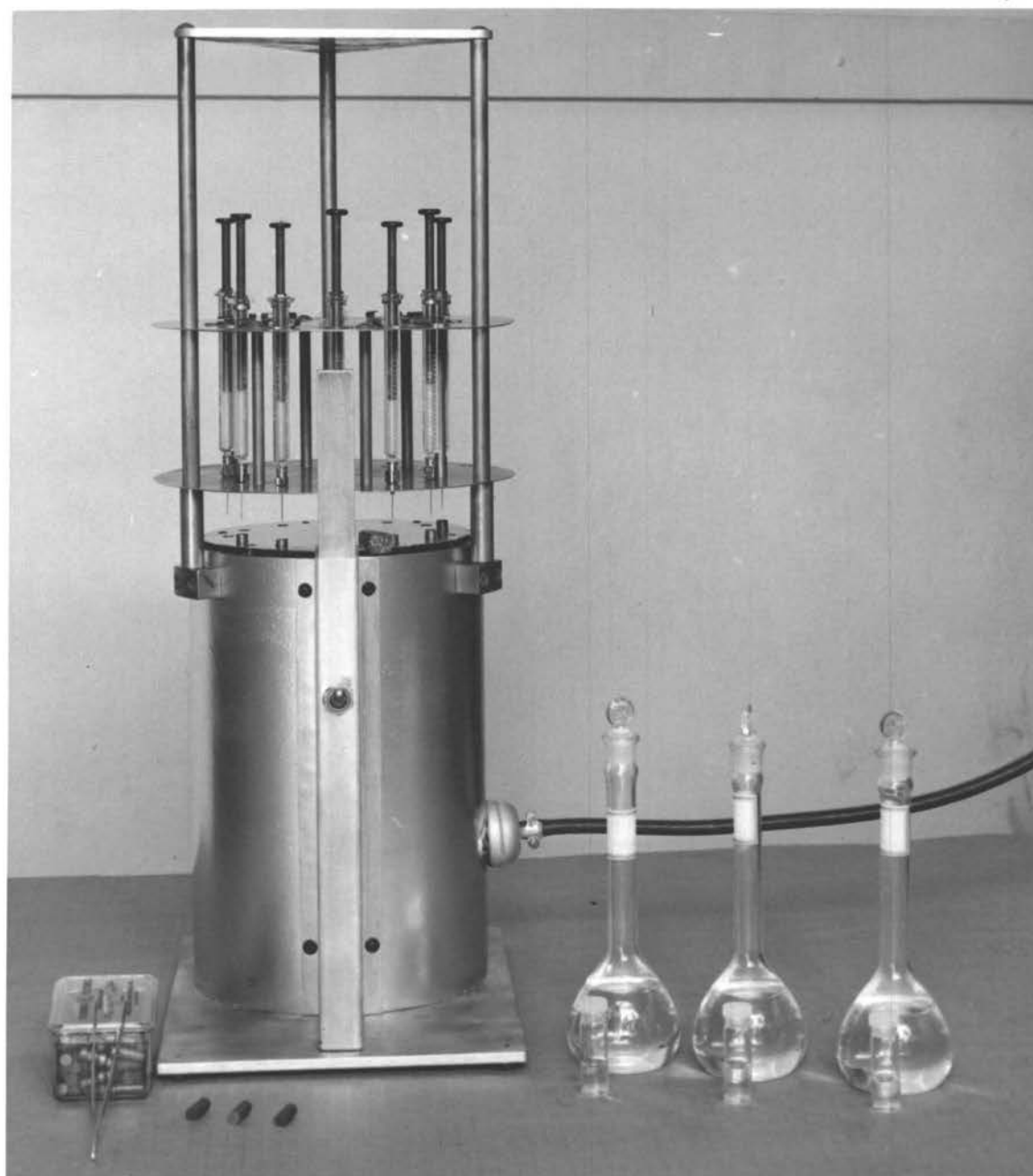


Fig. 3 Electrode Heater

The electrodes from which the solutions are to be evaporated are placed in the rack which forms the cover of the circular well. This rack is made from two stainless steel disks spaced $3/16$ " apart. The bottom ends of the electrodes rest on the solid lower disk, while regularly spaced $1/4$ " holes in the upper disk serve as guides to keep the electrodes upright. Heat is applied by an infra-red lamp located at the bottom of the well and oriented so that its reflecting surface is upward. The temperature of the electrodes is maintained between 85 and 90 degrees Centigrade by means of a bimetallic strip which actuates a microswitch in the lamp circuit. Evaporation of the liquid sample takes place quite rapidly without boiling and loss of sample in this range of temperature. The solutions to be evaporated are deposited on the appropriate electrode with the aid of the tuberculin syringes which are filled and placed in the rack directly above the electrode. The solutions may be deposited dropwise to the electrodes in rotation, thus resulting in economy of time. In this manner, about one milliliter of relatively non-volatile liquid, such as water, may be evaporated from each of twelve electrodes in an hour's time.

Excitation of Samples

The sample residue on the tips of the electrodes is excited by means of a 2400 volt alternating current arc

discharge maintained between the electrodes. A series of exposures, using standard samples, was made to determine the values of exposure, current, and electrode gap width giving optimum sensitivity and reproducibility. An exposure of 60 seconds, a gap width of 0.7 millimeters, and a current of 2.8 amperes gave the best results, and are consequently used throughout this work.

The importance of maintaining a fixed current and electrode gap width for each sample excited, has been demonstrated by Duffendack and Wolfe in their work on the spectrographic analysis of caustic liquors for metallic traces (8, pp.24-27). Therefore, considerable care is taken to accurately reproduce the excitation conditions given above. Since very little of the electrode material is burned away in the alternating current arc discharge, the electrodes are not adjusted during the arcing cycle, but are aligned and spaced properly just prior to the initiation of the discharge. Rapid and precise positioning of the electrodes is achieved with the aid of an enlarged image of the electrodes, formed on a wall chart some six or seven feet distant by an auxiliary light source and lens incorporated in the arc housing. The current is controlled during arcing by manual adjustment as necessary.

The general arrangement of the spectrograph slit, condensing lens and arc stand is shown in Fig. 4.

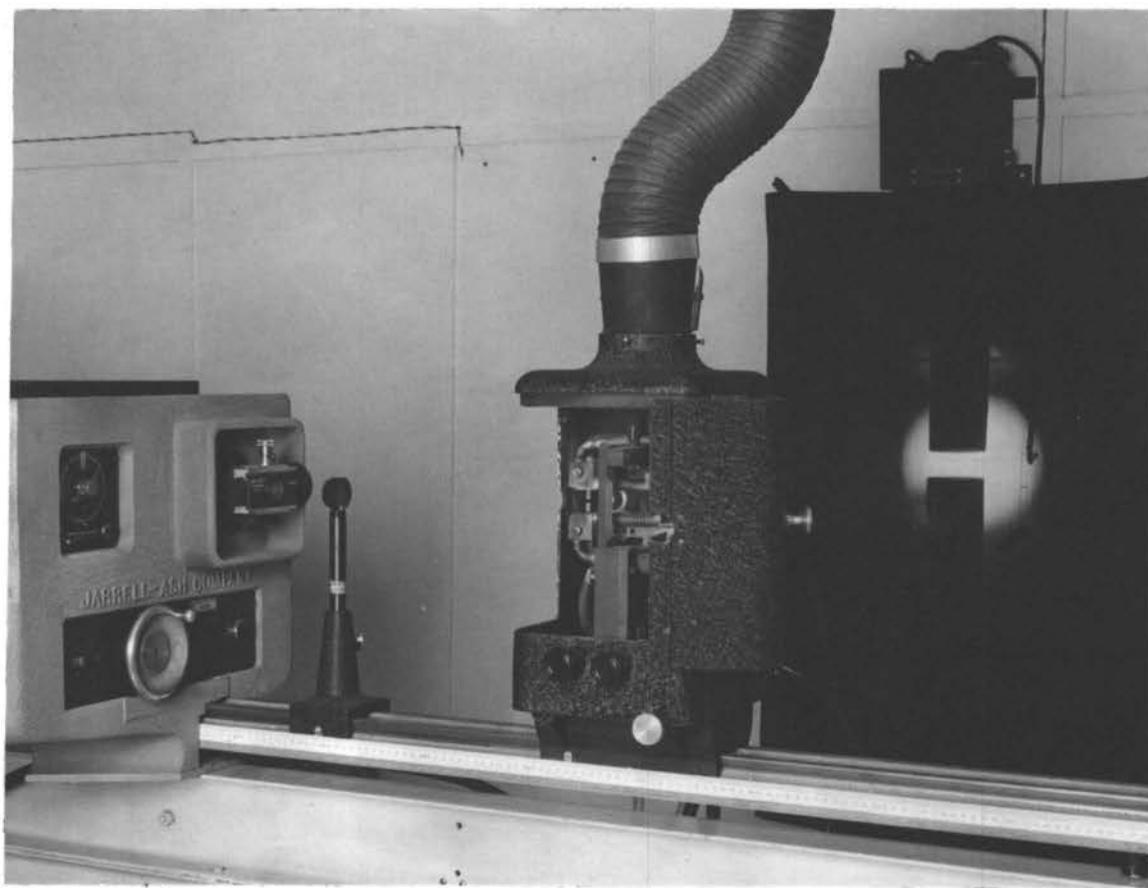


Fig. 4

In order to show the image of the electrodes on the wall as well as the interior arrangement of the arc housing, two exposures were made on the same piece of film. The first was made with the room lights off and the electrodes illuminated by the auxiliary light source so that their image was formed on the wall chart, while the second was made with the room lights on and the door of the arc housing open. The electrodes are separated a distance of 3 mm and are magnified approximately twelve times by the auxiliary lens.

Processing of Spectrograms

The spectra are recorded on Eastman Kodak Spectrum Analysis No. 2 photographic plates. This emulsion was selected for its high sensitivity, long scale, medium contrast, and relatively small grain size. The high sensitivity is important from the standpoint of detection of low sample concentrations, while the small grain size is desirable from the standpoint of reproducibility of density measurements of spectral lines. Since the concentration of silver in the rainwater samples, and hence, the intensity of the silver spectrum is expected to vary considerably from sample to sample, it is desirable to use a photographic emulsion capable of recording line intensities over a range of several orders of magnitude. The greater latitude of the medium contrast Spectrum Analysis No. 2 emulsion makes this possible and is thus preferred over higher contrast emulsions such as Spectrum Analysis No. 1.

After exposure, the photographic plates are developed for three minutes in undiluted Kodak D-19 developer at 20°C, rinsed in a 1% glacial acetic acid stop-bath solution for about 10 seconds, and fixed in acid hypo for 5 to 10 minutes. The plates are agitated continuously while in the developer and intermittently while in the stop-bath and hypo. The temperature of the processing solutions is controlled by the addition of either hot or cold tap water to a large volume water bath in which the trays of solutions are

partially immersed. After removal from the hypo, the plates are washed in tap water for approximately ten minutes, rinsed with distilled water, and allowed to dry in air at room temperature. The use of a sponge to remove excess water and the application of heat to speed drying resulted in the smearing and warping of this particular emulsion in some cases, and is to be discouraged. Development under the above conditions results in a gamma which does not vary appreciably from unity from plate to plate.

Evaluation of Spectrograms

1. Identification of Spectrum Lines. Rapid identification of the silver and tin lines in the spectrum of an unknown sample is accomplished by comparing the spectrum of the unknown with one contained on a master plate which has the proper lines labeled with the appropriate element symbol and wavelength. The master plate is prepared by recording an iron spectrum and the spectrum of a sample containing relatively large amounts of silver and tin adjacent to one another on a photographic plate. Several iron lines in the vicinity of the silver and tin lines are first located and identified with the aid of a detailed photograph of the iron spectrum appearing in the appendix of Brode (4, pp.447-482). The analysis and internal standard lines are then located by interpolation between these known lines and labeled for future use.

2. Densitometric Measurement of Spectrum Lines.

The response of the photographic emulsion to a given line intensity is measured by the Jarrell-Ash Company Microphotometer previously described. This measurement is made in terms of per cent transmission which is defined as the percentage of light transmitted by a photographic image, in this case a spectrum line, referred to the transmission of a clear unexposed portion of the emulsion taken as 100 per cent.

The per cent transmission of a given spectrum line is obtained by placing the exposed and processed photographic plate in the rack provided in the microphotometer, adjusting the galvanometer sensitivity so that its deflection is 100 divisions (corresponding to 100 per cent transmission) for a clear portion of the emulsion in the region where measurements are to be made, and recording the minimum galvanometer deflection obtained while moving the image of the spectrum line laterally across the photocell slit. Transmission readings of the continuum underlying both the analysis and internal standard lines are made adjacent to these lines. This background was found to remain essentially constant and very weak, always less than 95 per cent transmission, under the excitation and exposure conditions used in this method, and was consequently considered to be negligible. Therefore, no background correction is applied to the line intensities. It is, however, important to

check the background from time to time in order to be certain that it may be neglected. As a rule, background densities of the order of 0.1 (this corresponds to a transmission of approximately 80 per cent) may be ignored, if the background underlying both the analysis and internal standard line is essentially constant and if the general spectral background is fairly reproducible from one spectrum to another (14, p.136). Should a background correction be necessary, it should be made by subtracting the intensity of the background from the intensity of the line, thus giving the net line intensity.

3. Calibration of Photographic Emulsion. In the preceding section, the method for determining the response of a photographic emulsion, in terms of the per cent transmission of an image formed by incident light of a given intensity, was discussed. Since it is the intensity of an emitted spectrum line, not the per cent transmission of its image on a photographic plate, that is the measure of the amount of an element in a sample, it is necessary to establish the relationship between the two. Because these two quantities, per cent transmission and intensity, are not proportional over any appreciable range and furthermore cannot be represented by a simple function that can be expressed mathematically, their relationship must be determined from experimental data. This relationship between the intensity of light reaching a film and the resultant

photochemical response of the emulsion is variously termed the "photographic calibration curve," the "characteristic curve," the "D log E (density log exposure) curve," the "density curve," the "H and D (Hurter and Driffield) curve," or, more popularly, the "gamma curve."

(12, pp.49-50)

Data for the photographic calibration curves in the present work are obtained by the rotating sector method. In this method, a sector disk, such as that illustrated in Fig. 5, is mounted directly in front of the spectrograph slit and rotated at approximately 3500 rpm while the photographic plate is being exposed for 60 seconds by the light from an alternating current arc discharge of 4800 volts and 1.2 amperes between iron electrodes. Since the rotating sector continuously interrupts the light beam, a stepped or graded series of exposures along the length of the spectrograph slit is obtained with the exposure of successive steps being proportional to θ_1, θ_2 , etc. The rotating sector used here is a "Jaco" 65 whose successive angles obey the relation, $\log \theta_i / \theta_j = 0.2$, so that successive exposure steps are related by the expression $\log E_i / E_j = 0.2$ where E_i refers to the exposure through any angular opening and E_j to the exposure through the adjacent smaller angular opening.

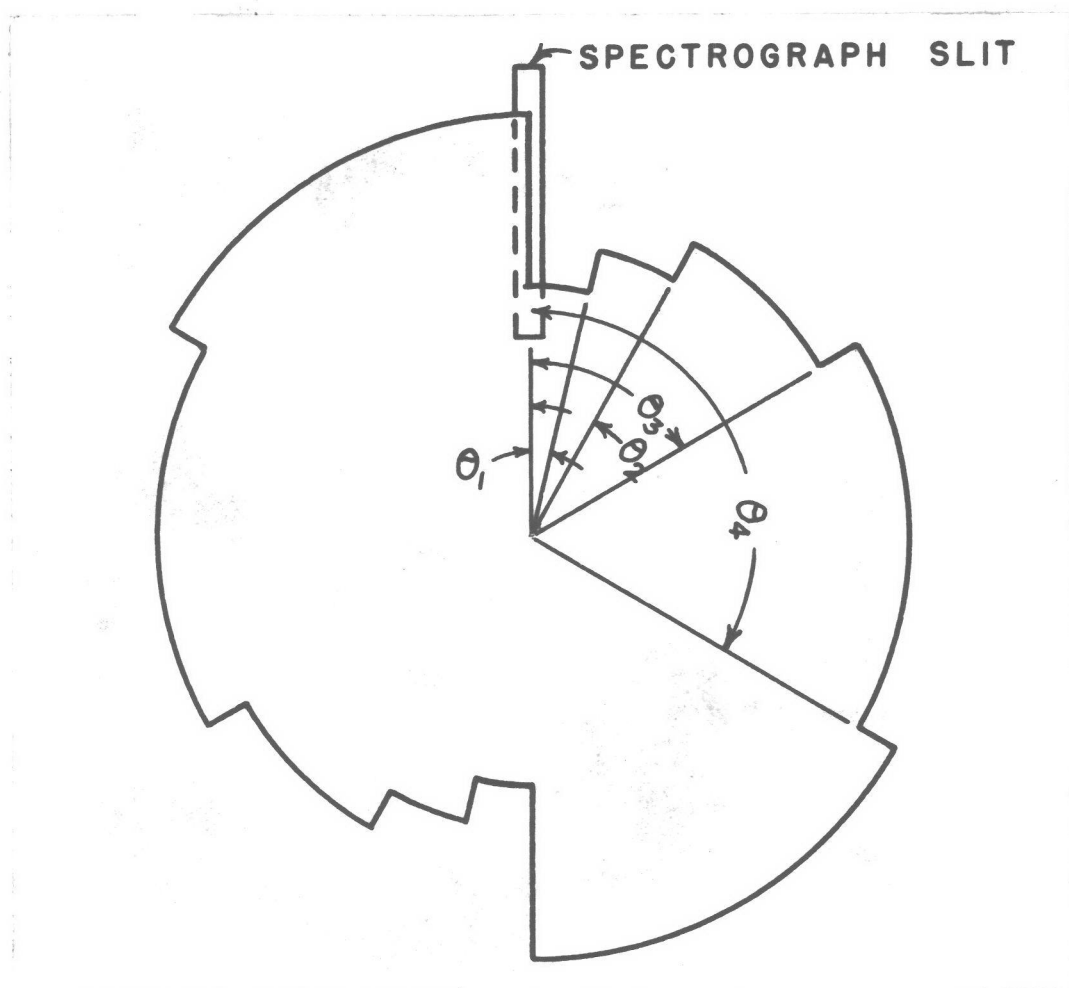


Fig. 5 Rotating Step-Sector

A photographic calibration curve may be obtained from this data by plotting the logarithm of the per cent transmissions of a particular iron line for each step versus the logarithm of exposure. However, since the ultimate function of the calibration curve is to relate the per cent transmission of a line image with the intensity of the light producing the image, it is convenient to replace the exposure values with relative intensity values on a purely

arbitrary scale, and to plot logarithm of per cent transmission versus logarithm of relative intensity. This procedure is, of course, invalid if absolute line intensities are required, but fortunately in this work as well as in other spectrographic methods based on the internal standard principle, all that need be known is the intensity ratio of the analysis and internal standard line.

In order to obtain a large number of experimental points so that the contour of the calibration curve may be accurately determined, a procedure described in detail by Harvey (12, pp.73-76) was followed. Per cent transmission readings of three iron lines of different intensity are taken and the data obtained are plotted as shown in Fig. 6. From this figure it may be observed that the Fe 3222.0 curve will come into coincidence with the Fe 3225.7 curve if the relative intensities of the points of the Fe 3222.0 curve are multiplied by the factor 0.84. In like manner, the Fe 3239.4 curve will come into coincidence with both the Fe 3225.7 curve and the displaced Fe 3222.0 curve if its intensities are multiplied by a factor of 0.41. The final photographic calibration curve drawn after the experimental points were shifted in the manner described above is shown in Fig. 7. The iron lines used were selected from a group whose intensities were determined under a variety of excitation conditions by Dieke and Crosswhite (5, p.428) and found to remain essentially

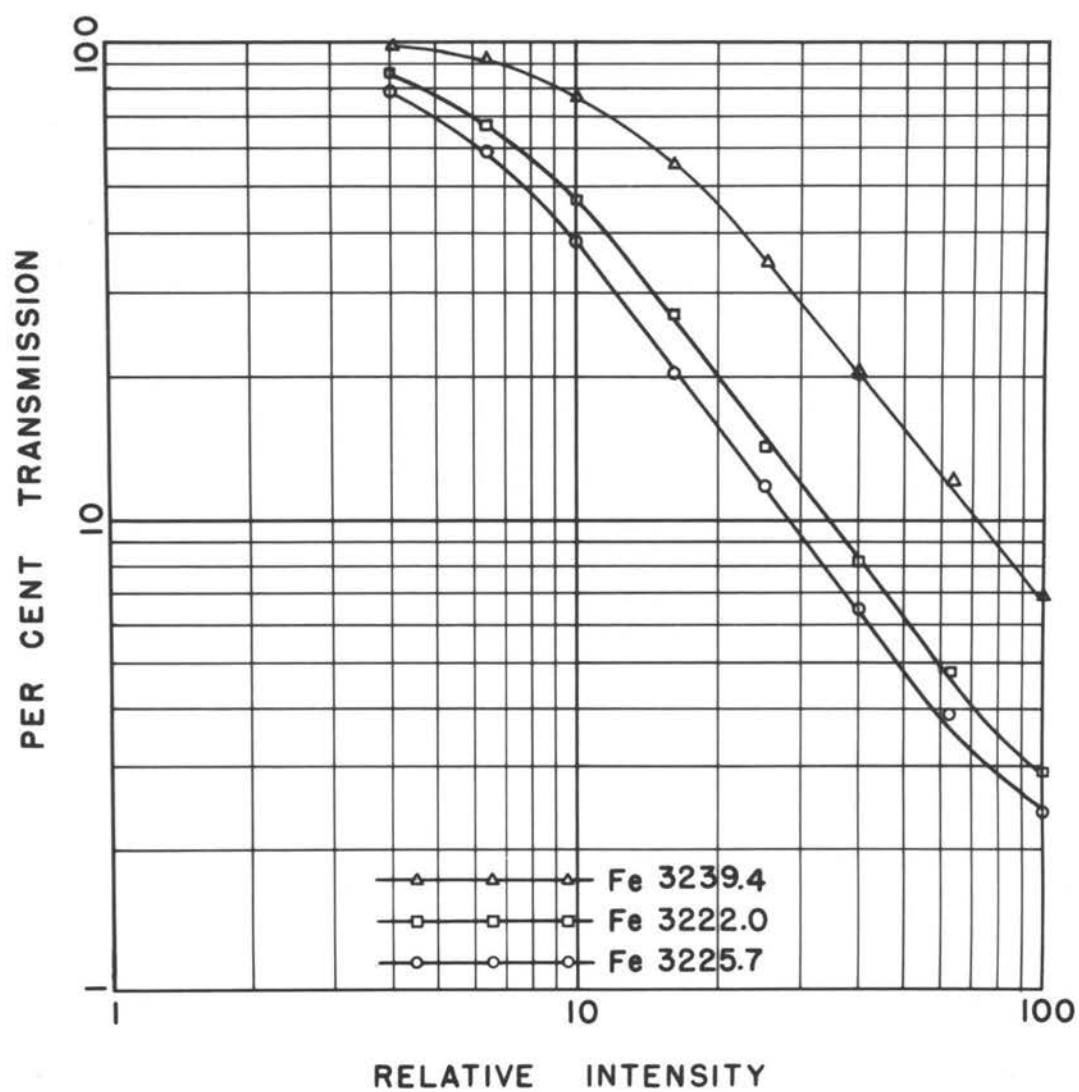


Fig. 6

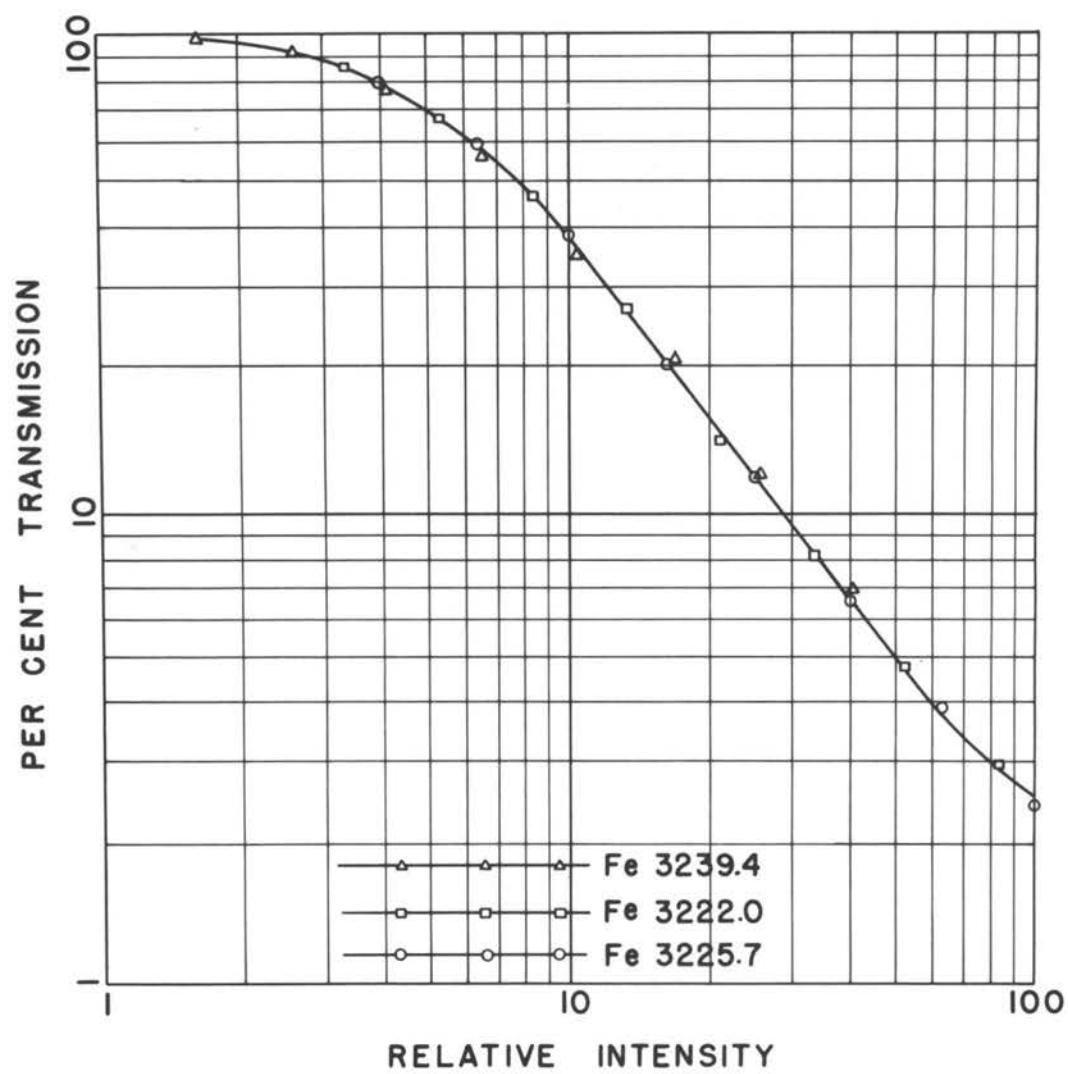


Fig. 7

constant and hence suitable for calibration purposes.

The possibility of incorrect calibration curves due to reflections and scattering of light in the spectrograph or in the microphotometer and the resulting necessity of using a calibration technique which gives self-consistent results with the equipment used has been discussed by Grossman, Sawyer and Vincent (11, p.186). The calibration method used in the present work was tested for self-consistency by a simple procedure described by Sawyer and Vincent in a later paper (16, p.247). Using this procedure it is only necessary to plot two calibration curves obtained by the method under test, from records on the same plate, made under identical conditions except that light intensity is varied between the two sets of observations. If the two curves, when plotted on the same coordinate axes, are translated into one another by a displacement parallel to the intensity axis, the calibration technique is self-consistent. Thus we see that the procedure used in the preceding paragraph for obtaining a large number of points in order to accurately determine the contour of the calibration curve, also may be used as a self-consistency test. The fact that the single curve in Fig. 7 results from a translation of the three curves of Fig. 6 into one another by displacements parallel to the intensity axis demonstrates the self-consistency of the calibration technique used.

Although the shape of the photographic calibration curve remained essentially the same for the Spectrum Analysis No. 2 emulsion used here, the slope of the straight line portion, called the "gamma" was found to vary somewhat from plate to plate. To rule out errors resulting from the use of a curve having the wrong slope, each photographic plate used was calibrated.

In order to simplify the calibration procedure and eliminate tedious, repetitious plotting of a large number of experimental points, the following scheme was used. A step-sectored iron spectrum is recorded on each photographic plate and the per cent transmission of the first, fourth and seventh steps of the Fe 3239.4 line are read and plotted on log-log paper. The calibration curve is drawn through these points with the aid of a template previously cut to fit data obtained from several iron spectra on the same plate and plotted as described in the previous paragraphs and illustrated in Figs. 6 and 7. In this manner, each plate is rapidly and precisely calibrated with a minimum of effort.

Preparation of Working Curve

The term "working curve," as applied in spectrographic methods based on the internal standard principle, refers to a graphical relationship between the concentration of the analysis element in a sample and the intensity

ratio of the analysis and internal standard lines. Intensity ratios of unknown samples are then referred to this curve to obtain the concentration of the analysis element.

The intensity of an emitted spectrum line of a given element is related to the amount of this element present in a sample being excited by the equation

$$I = KC \quad (3)$$

$$\text{or} \quad \log I = \log K + \log C \quad (4)$$

where I is the line intensity, C the concentration and K a constant. If the subscripts a and s refer to the analysis and internal standard elements respectively, we have for the intensity ratio of the analysis and internal standard lines

$$I_a/I_s = K_a C_a / K_s C_s \quad (5)$$

$$\text{or} \quad \log I_a/I_s = \log K_a + \log C_a - \log K_s - \log C_s. \quad (6)$$

Since the concentration of the internal standard is constant in each sample, Equation (5) may be rewritten as

$$\log I_a/I_s = B + \log C_a \quad (7)$$

where the constant factors in Equation (5) are replaced by the single constant B .

One form of working curve commonly employed in spectrographic methods is obtained by arcing a number of samples of known concentrations, and plotting the logarithm of the intensity ratios of the analysis and internal standard lines versus the logarithm of the concentrations of the analysis element. It is evident from Equation (7) that

the resulting curve should be a straight line with unit slope. A working curve of this type was used in the present work.

A series of samples of known silver concentrations are prepared and excited in the manner described in earlier sections of this paper and their spectra recorded on a photographic plate. A calibration spectrum is then recorded on the plate, the plate processed, and the emulsion calibrated. The analysis line Ag 3280.7 and the internal standard line Sn 3262.3 on each sample spectrogram are located and densitometered. The percent transmissions of the silver and tin lines are converted to relative intensities through the use of the calibration curve and their intensity ratio obtained. Finally, these intensity ratios are plotted versus the concentration of silver in parts per million on log-log paper, yielding the curve shown in Fig. 8. This curve is essentially a straight line, having a slope of approximately 41 degrees, and agrees favorably with the curve expected from theoretical considerations. The minor departure of the slope from unity indicates that the presence of background, self-absorption and residual impurity in the standard samples is negligible in the concentration range covered.

Theoretically, the lower limit of detection is restricted only by the amount of solution available for evaporation on the electrodes. However, a practical lower

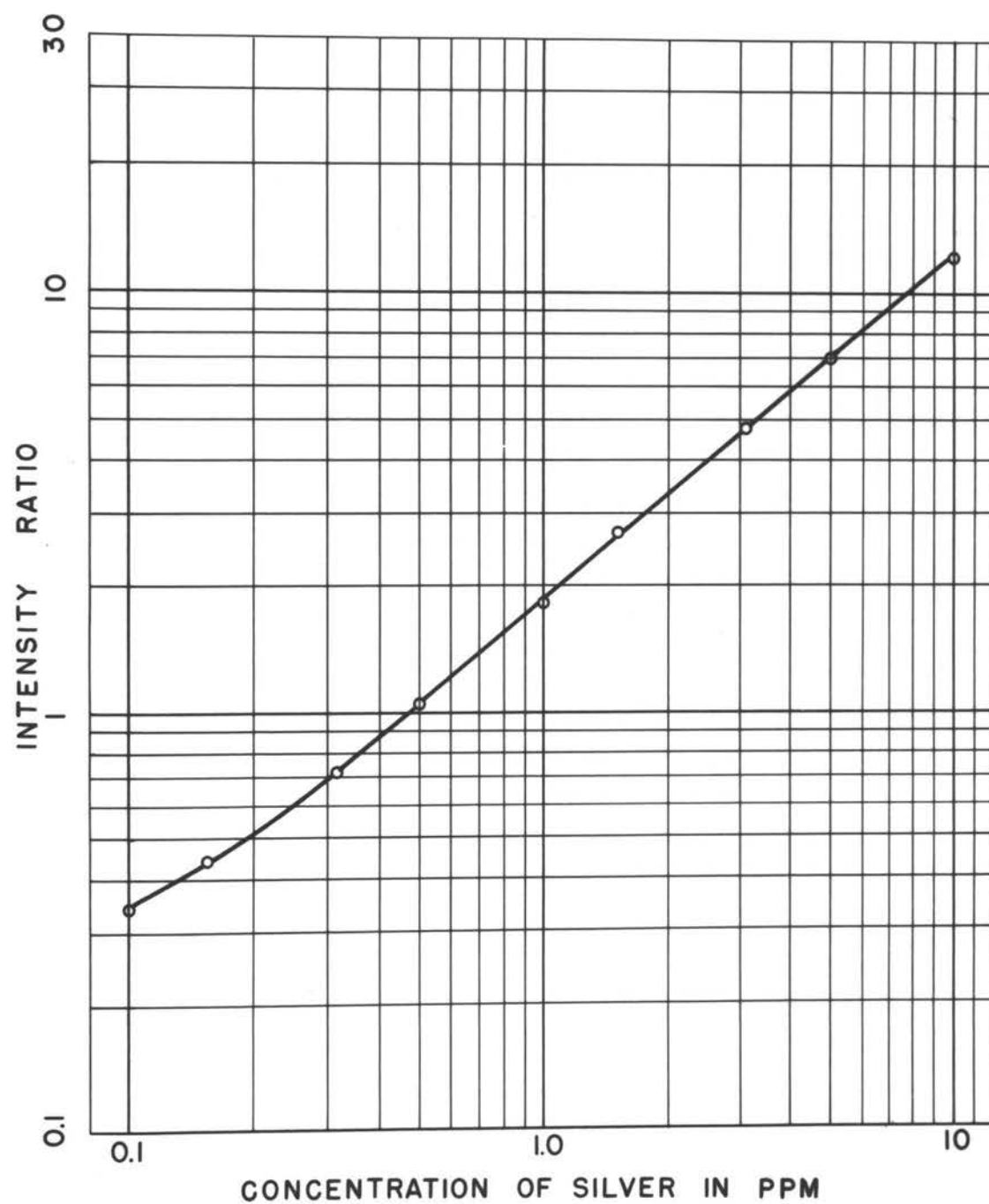


Fig. 8

limit of 0.1 ppm is imposed on the method due to random contamination and residual impurities in the reagents used. Considerable work was done with solutions less than 0.1 ppm in concentration, and in some cases concentrations of the order of 0.01 ppm were detected. However, results in this range are quite questionable due to the reasons mentioned above.

ANALYSIS OF RAINWATER SAMPLES

Introduction

The rainwater samples submitted for analysis were received by parcel post from various collecting locations throughout the states of Oregon and Washington. Collection and shipment of the samples were made in one pint capacity, wide mouth, glass fruit jars, of the type used for home canning purposes. Of the one hundred and twenty-five containers received, fourteen were broken enroute and thirty-three were completely dry.

A preliminary inspection of the containers received intact and containing liquid sample revealed two disturbing factors which, in the opinion of the author, will seriously limit if not prevent entirely any interpretation of the results of the spectrographic analysis as to the effectiveness of seeding clouds with silver iodide: (1) The rainwater samples were, almost without exception, extremely dirty with respect to foreign matter which was probably introduced during collection. Most of the foreign matter appeared to be small particles of soil or vegetation; however, leaves, twigs and even insects were present in some containers. It appears quite likely that contamination from these impurities could completely mask the presence of the minute silver traces expected from the silver iodide particles. (2) The manner of collection of samples was

such as to make definite determination of the volume or weight of the original rainwater sample impossible. The rainwater was collected by simply allowing the containers to stand outdoors with their covers removed for one week's time. It is reasonable to assume that, during this time, evaporation of the collected sample was appreciable, especially during periods between showers. If evaporation does take place, it is expected that the spectrographically determined silver content will be too high by an undetermined factor due to concentration of the sample by the evaporation process. It is extremely unfortunate that adequate precautions were not taken to prevent or at least minimize these difficulties. For any future work contemplated in this field, the author strongly recommends that collection procedures be modified and standardized to achieve representative and uniform samples.

Since nothing could be done to eliminate these difficulties after the samples had been received, it was decided to proceed with the analysis, keeping in mind the very strong possibility of erroneous results due to the causes discussed above.

Sample Preparation

After unpacking, the sample containers are thoroughly cleaned on the outside, their lids removed, and sample and container weighed to within one-tenth of a

gram on a platform balance. The containers are then placed under a bank of infra-red lamps and the sample evaporated to dryness. The containers are again weighed and the original weight of the liquid sample computed. Ten milliliters of a standard stock solution of acetone containing one part per million tin by weight and 0.2 milligrams of potassium iodide per milliliter is then added to the residue in each container. Silver iodide is extremely insoluble in pure acetone; however, it is fairly soluble in a solution of acetone and either potassium or sodium iodide. For exact figures, the reader is referred to Seidell (17, p.59).

Therefore, any silver iodide present in the sample residue will be dissolved by the acetone and potassium iodide solution. This rather simple treatment given the samples not only results in a concentration of the original sample, but also transforms the original sample into a homogeneous solution of silver containing a constant amount of tin as an internal standard. These solutions are then run in duplicate in a manner identical to that used for the standard samples employed in the construction of the working curve.

Periodic shifts of working curves, attributed to variations in temperature and humidity by many spectrographers, are a common experience in spectrographic laboratories (12, p.247). To compensate for such shifts which were observed in the present method, two standards of

concentrations 10 and 0.1 parts per million silver are run along with the unknown samples on each photographic plate. Using a spectrograph slit length of two millimeters, it is possible to record the duplicate spectrograms of sixteen unknown samples and two standards and a step-sectored iron spectrum on one 4 x 10 inch photographic plate.

Calculation of Unknown Concentrations

After the photographic plate is processed and calibrated, the Ag 3280.7 and Sn 3262.3 lines of each spectrogram are densitometered and the resulting per cent transmission readings converted to relative intensities through the use of the calibration curve. The ratio of the intensity of the Ag 3280.7 line and the intensity of the Sn 3262.3 line is then calculated for each standard and unknown sample. The intensity ratios, obtained by averaging the duplicates of each standard sample, are plotted against their corresponding concentrations on the working curve axes and the working curve shifted so that these points lie on it. Once the working curve has been standardized in this manner, the intensity ratios of the unknown samples may be referred to the curve to obtain the corresponding concentration of silver in parts per million. It must be remembered that the concentration of silver obtained directly from the working curve refers to the

parts per million by weight in the 10 milliliters of acetone and potassium iodide solution added to the dry residue of each rainwater sample. Since the ultimate purpose of the analysis is to determine the concentration in the rainwater itself, it is necessary to relate the above concentrations to the weight of the original rainwater sample. If C_r and C_a denote the concentration in parts per million by weight in the rainwater and acetone respectively, and W_r and W_a the respective weights of the original volume of rainwater and the volume of acetone added to the sample residue; the concentration of silver in the rainwater is given in parts per million by

$$C_r = C_a W_a / W_r, \quad (8)$$

or, since the weight of 10 milliliters of acetone at room temperature is 7.92 grams,

$$C_r = 7.92 C_a / W_r. \quad (9)$$

Analytical Results

1. Concentration of Silver in Typical Samples.

The results of several typical samples analyzed by the method developed in this paper are tabulated in Table 1. The results represent the average of two separate arcings.

2. Precision. After the development of a spectrographic method, it is desirable to make some statement as to its reproducibility or precision. The precision of this

<u>SAMPLE NO.</u>	<u>LOCATION</u>	<u>W_a (grams)</u>	<u>C_a (ppm Ag)</u>	<u>C_r (ppm)</u>
1-B	Astoria, Ore.	192.7	0.44	0.018
2-B	Moro, Ore.	11.0	0.77	0.55
3-B	Pendleton, Ore.	65.9	1.2	0.14
4-B	Condon, Ore.	-	Insufficient sample	
5-B	Heppner, Ore.	-	Container broken	
6-B	Hyatt, Ore.	232.7	1.69	0.054
7-B	Medford, Ore.	-	Insufficient sample	
8-B	Four-Mile Cutoff, Ore.	197.3	0.59	0.024
9-B	Seattle, Wash.	110.6	1.8	0.13
10-B	Ellensburg, Wash.	76.1	1.6	0.17
11-B	Crater Lake, Ore.	83.0	3.1	0.30
12-B	Baker, Ore.	-	Insufficient sample	
13-B	Portland, Ore.	105.5	1.3	0.098
14-B	Lakeview, Ore.	-	Insufficient sample	
15-B	Burns, Ore.	64.8	0.16	0.020
16-B	Bend, Ore.	32.3	0.70	0.17
17-B	Fish Lake, Ore.	81.4	0.22	0.021
18-B	Spokane, Wash.	3.7	0.48	1.03
19-B	Klamath Falls, Ore.	86.8	0.89	0.081
20-B	Boise, Idaho	1.3	0.22	1.3
21-B	Gold Beach, Ore.	294.4	0.44	0.012

Table 1

method was investigated by performing twelve individual analyses on a typical sample and computing the standard deviation. A sample whose concentration was approximately mid-range of the method was used. Results are tabulated below.

<u>Analysis No.</u>	<u>C_a(ppm Ag)</u>	<u>Deviation</u>	<u>(Deviation)²</u>
1	0.41	-0.01	0.0001
2	0.43	+0.01	0.0001
3	0.41	-0.01	0.0001
4	0.40	-0.02	0.0004
5	0.40	-0.02	0.0004
6	0.42	-	-
7	0.43	+0.01	0.0001
8	0.46	+0.04	0.0016
9	0.40	-0.02	0.0004
10	0.44	+0.02	0.0004
11	0.44	+0.02	0.0004
12	0.37	-0.05	0.0025
Average	0.418		0.0065

The per cent standard deviation is computed from the equation $S = \frac{100}{\bar{C}_a} \left(\frac{\sum_{n=1}^k d_n^2}{k-1} \right)^{\frac{1}{2}}$; where d is the deviation, k the number of determinations and \bar{C}_a the average concentration.

A standard deviation of 5.8% is obtained from the data above. On the basis of an arbitrary scale suggested by Ahrens (1, p.85), the reproducibility of the method would be considered good.

DETAILED PROCEDURE FOR ANALYSIS OF RAINWATER SAMPLES

Sample Preparation

Weigh container and rainwater sample

Evaporate sample to dryness under infra-red lamp

Weigh container and determine weight of original volume of rainwater

Add 10 ml of acetone stock solution to sample residue and agitate thoroughly

Prepare four electrodes for each sample by depositing the acetone solution dropwise to each electrode in rotation until lcc has been deposited and evaporated on each

Excitation

Unknown samples and standards

Source 2400 volt A.C. arc

Current 2.8 amps

Arc gap 0.7 mm

Exposure 60 sec (No pre-arc)

Iron calibration spectrum

Source 4800 volt A.C. arc

Current 1.4 amps

Arc gap 5 mm

Exposure 60 sec (No pre-arc)

Optical System

Unknown samples and standards

Arc stand at 63.2 cm

67 cm quartz cylindrical condensing lens at
30.5 cm

Slit width 25 microns

Slit height 2 mm

Spectral region 2250 - 4000A

Iron calibration spectrum

Step-sector at 30.5 cm

Slit height 12 mm

Other items remain the same as above

Emulsion

Spectrum Analysis No. 2 plate loaded on right side
of cassette

Plate Processing

Develop 3 minutes in undiluted D-19 at 20°C

Rinse 10 seconds in 1% glacial acetic acid solution

Fix 5-10 minutes in acid hypo

Wash 10 minutes in tap water

Rinse with distilled water and dry

Photometric Measurements

Locate the Ag 3280.7, Sn 3262.3, and Fe 3239.4
lines by comparison with the master plate

Densitometer the Ag 3280.7 and Sn 3262.3 lines of
each sample spectrogram and the first, fourth,
and seventh steps of the Fe 3239.4 line of the
iron calibration spectra

Calculations

Plot the calibration curve and convert all per cent transmissions to relative intensities

Compute the intensity ratios, $\frac{I_{Ag3280.7}}{I_{Sn3262.3}}$, for each sample

Adjust the working curve with the aid of the standard ratios

Determine the concentration of silver in the acetone solutions from the working curve and convert these concentrations to concentration of silver in the original rainwater sample by the formula

$$C_r = 7.92 C_a / W_r$$

where C_r is the concentration in rainwater, C_a the concentration in acetone and W_r the weight of the original rainwater sample. Concentrations obtained in this manner are given in parts per million

SUMMARY

A spectrographic method for the determination of silver in rainwater using tin as an internal standard has been developed and applied to a series of typical samples. The equipment used includes a 4.8 meter grating spectrograph, commercial power supply, comparator microphotometer, and other minor equipment as described in the main body of this paper.

The rainwater samples are converted to acetone solutions and evaporated directly on flat-topped graphite electrodes, which are excited in a high voltage alternating current arc discharge. The Ag 3280.7 and Sn 3262.3 lines are used as the analysis and internal standard lines respectively. Calibration of the Spectrum Analysis No. 2 emulsion used is accomplished by the use of a step-sectored iron spectrum recorded on each plate.

The concentration range covered by this method is from 0.1 to 10 parts per million silver by weight in the acetone solutions. The standard deviation at a concentration of 0.5 parts per million is 5.8%.

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