

T H E S I S

on

Determination of Iodine in Kelp

Submitted to the Faculty

of the

O R E G O N A G R I C U L T U R A L C O L L E G E

for the degree of

Batchelor of Science

by

Redacted for Privacy

Redacted for Privacy

Approved

Redacted for Privacy

Redacted for Privacy

Department of

THE DETERMINATION OF IODINE IN KELP.

Among sea-weeds the kelps include some of the largest, most widely distributed and most important forms considered from an economical standpoint. They are technically classified among the brown algae in the family Laminariaceae, which comprises some twenty-five genera. Kelps occur most abundantly in the colder sea water, but they are very poorly developed, or altogether absent, in tropical oceans. In the circumpolar regions, both north and south, they find their best and most favorable habitats. Many of the genera are either monotypic or with but a limited number of species. *Alaria*, with upward of twenty species and *Laminaria*, with more than thirty are the largest genera, and these are also most widely distributed. The region of the Pacific coast of North America exhibits the largest numbers of monotypic genera, and may be considered as the most promising coast in the world for study of these forms both scientifically and economically.

Kelp by some authorities is considered as belonging to a certain class of sea-weeds of the class Algae, family Laminariaceae; others classify it as a

product of incineration of certain sea-weeds; while still others make no such close distinction. In this short thesis kelp will be considered the product of incineration from which the sea-weeds were nicknamed.

Kelp is produced by the incineration of various kinds of sea-weeds belonging to the class of Brown Algae, family Laminariaceae, common along the coast. Many of the species are of large size, ranging from six to ten feet in the "Devil's Apron" of the Atlantic Coast of North America to several hundred feet in the giant kelp of the Pacific Ocean.

They are composed of considerably differentiated tissues, and are simple and leaf-like or more commonly subdivided.

Kelp is gathered commercially along the west coast of Ireland and Scotland and the coast of Brittany in France. A ton of kelp is obtained from about twenty to twenty-two tons of wet sea-weed.

The best weeds gathered are those of deep water and they are only obtainable when cast ashore by storms or other causes. This is known as "drift-weed kelp" and yields about .46% iodine. Cut weeds are those which grow in shallow water so as to be cut at low tide and yield about .07% iodine.

Previous to the Leblanc process for the manufacture of sodium carbonate, kelp was the principal source of potassium salts, and consequently was a raw

material of much importance in chemical industries.

About the beginning of the nineteenth Century the value of the Kelp prepared on the coast and islands of west Scotland, which was the principal source, was not less than one million dollars per annum. With the gradual introduction and improvement of the Leblanc process, and the reduction of duty on salt and other causes, the value of kelp decreased from one hundred dollars and upwards to about ten dollars per ton, a price altogether unremunerative. Toward the middle of the century, however, a new impetus was given to the trade by the rise of the manufacture of iodine of which kelp was at first the only commercial source.

The introduction of Chili saltpetre (caliche) as a source of iodine and the development of Strassfurth mines for potash salts have in their turn had a depressing influence on the kelp industry, and it is only by the most careful utilization of all the salts contained in kelp, and the use of the most approved methods of preparing the material, that the industry is continued as a remunerative undertaking.

With these facts in view, American labor of common class gradually getting to a level of European, the steady increase for potassium salts and iodine, and their rise in price, it is only a matter of time until we shall be able to start a well paying industry on our own coasts.

Iodine was discovered by Courtois in 1812, who observed that a beautiful violet vapor was evolved, during his endeavors to prepare nitre from liquors obtained by lixiviating the ashes of burnt sea-weed. Davy and Gay-Lussac showed iodine to be an element, and established its relationship to chlorine.

Like all the other members of the halogen group of elements, iodine is never found in nature in the uncombined condition. In combination it occurs associated principally with potassium, sodium, magnesium and calcium as an iodide or iodate.

Iodine is a widely distributed element, although not occurring in more than small quantities in any particular source. Thus it is found in small quantities in sea-water and in both marine plants and animals. The amount of iodine in sea-weed varies with different plants; generally speaking, those of greater depths, contain more than weeds which grow in comparatively shallow waters.

In small quantities, iodine is present in natural sodium nitrate of Chili and Peru, known as 'Chili-saltpetre' or 'caliche', chiefly as sodium iodate. According to Nöllner the iodine occurs from the formation of the 'caliche' in the presence of decaying seaweeds from shallow, stagnant, inland seas, which have dried up. Although the amount of iodine in 'caliche' is only small, averaging about .2% in view

of the enormous quantity of nitrate that is turned out, the aggregate amount of iodine is very great. The iodine is now extracted, and the supply of this element that is now manufactured from this source practically supplies the world.

Iodine has an atomic wieght of 126.85, oxygen at 16, is electro-negative, and has a specific gravity of 4.95. It is a black-grey colored crystalline substance, with a metallic appearance not unlike graphite. The absorption-spectrum of iodine vapor shows numerous fine lines extending from the red to the violet. As the thickness of the layer increases, absorption becomes very marked in the red; but even when the whole of the red part is obscured, the violet portion remains without bands. (Plücker, Thalen, Conroy and Salet). The emission-spectrum shows many bright lines in the yellow-green and yellow. By using an induction-current of low tension, lines are seen coincident with the dark absorption lines. (Salet and Wüllner). At a red heat continous spectrum is observed. On being heated iodine is converted into vapors which according to Stas, when concentrated exhibit a blue color and a violet in a more dilute state.

Iodine fuses at 115°C and boils at 200°C. It is somewhat soluble in water, readily soluble in alcohol, benzol, Carbon disulphide, aqueous solution sulphurous acid and a solution of sodium thiosulphate.

Iodine is largely used in medicine and photography combined as iodine of potassium; for the preparation of other iodine compounds as iodide of mercury; also in preparations of some of the coal tar colors as iodine-violet and iodine-green.

The only two practical methods of getting the seaweed reduced that it may be made to yield its iodine--the old method of incineration and then lixiviation of the ash or kelp with water--proved to be far more efficient and economical than Stanfords method of boiling the weed with sodium carbonate after which it is filtered. The filterate is known as algulose, to this is added hydrochloric acid which percipitates a compound known as alaginic acid, again filter and neutralize with sodium hydrate, evaporate to dryness and carbonize, which leaves a residue called "kelp substitute" supposed to contain all iodine and potash salts but was found not to be as reliable with different weeds as the former or old method.

The method used here to determine the amount of iodine present in the kelp, and found to be very accurate under known conditions, consists of concentrating the solution after incineration and lixiviation. Acidify this with acetic acid, add hydrogen peroxide (three percent solution, one cubic centimeter to the gram of iodine present) and allow to stand about half an hour. Wash out the iodine with chloroform, wash the chloroform with water to remove any hydrogen peroxide that may be

present and titrate with sodium thiosulphate with or without starch as an indicator; better however for very weak solutions to use the United States Pharmacopoeia test solution of starch.

The fault of other methods lies in the fact that they are affected by the presence of other compounds found to be present such as chlorides, bromides, sulphates, carbonates, sulphides and organic acid radicals of the alkalies which are all soluble in water.

The following are results of several samples obtained from Newport Oregon and several from the Oregon and Washington coasts about fifteen or twenty miles each way from the mouth of the Columbia river, shipped from Oysterville, Washington.

Sample 1.

Newport Oregon.

	Cut-weed. (a)	(b)
Sample -----	3.49 gm.	4.06 gm.
50/n $\text{Na}_2\text{S}_2\text{O}_3$ -----		-----
Percent iodine	None present.	

Sample 11.

Cut-weed.

	Oysterville. (a)	Washington. (b)
Sample -----	9.59 gms.	11.08 gms.
50/n $\text{Na}_2\text{S}_2\text{O}_3$ -----	.3 c c.	.35 c c.
Percent iodine -----	.0078.	.0079.

Sample 111.

Drift-weed (not a kelp variety).

	Newport, Oregon. (a)	(b)
Weed -----	2.18 gms.	-----
-----		-----
-----	None present.	-----

Sample 1V.

Drift-kelp.

	Newport, Oregon. (a)	(b)
Sample -----	5 gms.	5 gms.
50/n $\text{Na}_2\text{S}_2\text{O}_3$ -----	8.6 c c.	8.5 c c.
Percent iodine -----	.433.	.428.