3. The treatment with nitric acid of hydrogen electrodes which had been plated in solutions containing lead was found to be unnecessary. Thinly platinized electrodes give practically the same potentials as thickly coated ones.
4. The oxidation–reduction potentials of the ferric–ferrous electrode have been determined at various acid concentrations. It is to be emphasized that these values are of practical importance in attempting to make predictions.
5. The normal oxidation–reduction potential determined in this study compares favorably with the potential calculated from equilibrium measurements by Noyes and Brann.
6. The principle of ionic strength was applied to the calculation of the normal potential employing data obtained in 0.05 molal hydrochloric acid. The values thus calculated are in fair agreement (considering the uncertainty of activity coefficients now available) with that derived by extrapolation.
7. The value for the normal oxidation–reduction potential of the ferric–ferrous electrode determined in this study is -0.7477. The uncertainty is probably of the order of ±0.5 mv.

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[CONTRIBUTION FROM THE PHYSIOLOGICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF MINNESOTA AND THE SOUTH CAROLINA FOOD RESEARCH COMMISSION LABORATORY IN AFFILIATION WITH THE MEDICAL COLLEGE OF THE STATE OF SOUTH CAROLINA]

THE DETERMINATION OF TRACES OF IODINE. II. IODINE IN VEGETABLES[1]

BY J. F. McCLENDON AND ROE E. REMINGTON[2]

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In the first paper of this series[3] the general principles of a method for the determination of traces of iodine were outlined. The statement was made that an apparatus for feeding in milk powder was used. This apparatus is also useful for vegetables and consists of a steel tube with water-cooled open end and piston in the other end which is advanced by means of a screw similar to the piston of an "Alemite gun." Vegetables are made into a stick, placed in the steel tube, and advanced slowly by means of the screw and thus fed into a silica tube furnace and burned in oxygen.

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[1] This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council of Pharmacy and Chemistry, American Medical Association.

[2] With the technical assistance of F. B. Culp.

[3] McClendon, THIS JOURNAL, 50, 1093 (1928).

Original Procedure

An outline of the apparatus is given in Fig. 1. The steel tube is of 24 mm. bore and 50 cm. long. The walls are 1 mm. thick and the threads on the screw are 2 mm. apart (pitch). Around the open end is coiled 10 turns of lead pipe, 3 mm. bore for cooling-water. The steel tube is clamped rigidly in a horizontal position. Its open end is applied to the open end of a horizontal silica tube of 36 mm. bore and 60 cm. long with an elbow extending downward of the same bore and 30 cm. long.

The horizontal portion of the silica tube is heated by five large Méker burners. Around the junction of the steel tube with the silica tube is a pyrex glass adapter of 38 mm. bore with a side neck admitting oxygen and allowing the oxygen to go into a small crack between the steel and silica tubes. The elbow of the silica tube extends downward into an absorption flask made of three 500-cc. pyrex globe flasks. In the absorption flask is placed 0.25 g. of sodium hydroxide and enough water to extend into the middle section or second globe. Some of this solution is run into the 4 Milligan wash bottles (connected in parallel) by tilting the flask. The space between the elbow and the lip of the absorption flask is stoppered with wet asbestos. The absorption flask and Milligan wash bottles stand in a tank full of ice water. The side neck of the absorption flask passes to the Milligan wash bottles and then through a small Cottrell precipitator (described in the first paper) and to a rapid air pump (Cenco rotary No. 1400) which exhausts the air at the rate of 1.25 cu. ft. per minute and causes the oxygen to flow into the open end of the silica tube.

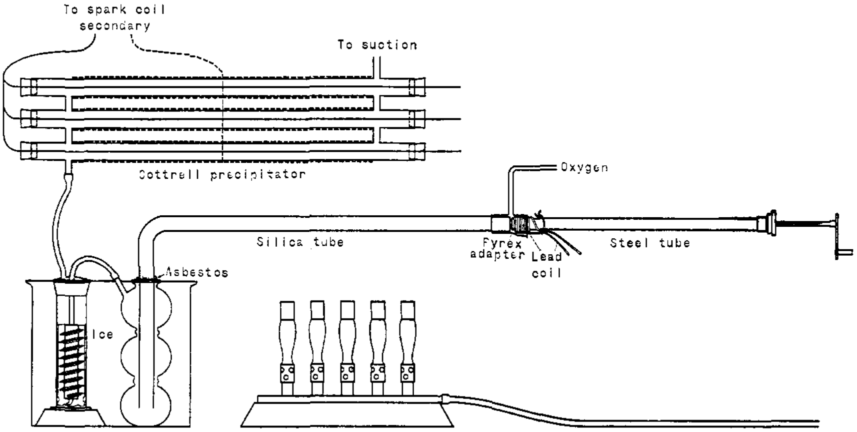

Fig. 1.

About 5 to 10 kg. of the fresh vegetables to be analyzed are ground in a suitable mill and the pulp partially dried on sheets of tin, or cheap dinner plates, in an electric oven at about 100°. When the pulp reaches the consistency of putty, it is made into sticks about 50 mm. long and 24 mm. in diameter and replaced in the oven. The sticks shrink in length and diameter during further drying. In starting the combustion a stick is placed in the steel tube and the screw advanced until a few mm. of the stick extends out of the steel tube. The oxygen is turned on, the Méker burners are lighted, the pump is started and the Cottrell precipitator operated. The oxygen adapter is slid to one side and a gas flame is applied to the crack between the steel tube and the silica tube until the stick of vegetable material is ignited. The adapter is quickly replaced so that the stick burns with a white heat in oxygen. The stick is advanced by means of the screw at such a rate that it burns without the evolution of soot and tarry material. It is usually possible to advance it about 0.5 mm. per second unless it contains a great deal of fat or oil, in which case it may not be possible to advance it so rapidly. The rate of advance depends also on the rapidity of the pump, it being understood that oxygen is fed in as fast as it is sucked through by means of the pump. The ash is drawn a few cm. into the tube by the current of flue-gas. After the completion of the burning of one stick, another one is placed in the steel tube without stopping the rest of the apparatus and burned in the same way, this process continuing until the whole sample has been burned.

At the end of the combustion the contents of the large absorption flask and the wash bottle and washings of the Cottrell precipitator are evaporated in a pyrex beaker. The ash is scraped out of the silica tube and ground with the washings of the tube in a small ball mill using Jasper balls (from the Jasper Stone Company, Jasper, Minnesota). After grinding for several hours and until the ash is reduced to an impalpable powder, it is removed from the ball mill to a centrifuge tube or beaker, allowed to settle or centrifuged and the soluble portion transferred quantitatively by several decantations to the beaker containing the contents of the absorption flask. When the contents of the beaker have evaporated to a small volume, they are transferred to an evaporating dish, dried in an electric oven to dryness and then scraped out with a steel spatula, ground in a mortar and placed on a curved piece of sheet nickel which is placed in a pyrex combustion tube of about 30 mm. bore and 40 mm. long with an elbow which is drawn out to a much smaller bore, 20 mm. long and extends down into a side-necked test-tube. In the test-tube are placed a few milligrams of sodium hydroxide and 10 cc. of distilled water. The space between the lip of the test-tube and the elbow is plugged with wet asbestos. A suction pump is attached to the side neck. The region under the nickel boat is heated with a large, flat gas burner with the air vent opened just enough to prevent the flame from being luminous or, in other words, the pyrex tube is heated just below its softening point while air is drawn through the tube. The open end of the tube is loosely plugged with a ball of dry asbestos or glass wool so as to prevent convection currents. The heat is continued until the traces of organic matter which have escaped the first combustion are entirely burned. It is rarely necessary to redissolve the ash, filter it and burn the carbon separately. The heat of the tube should not be high enough to fuse the ash, as that will stop the combustion.

At the end of the second combustion the ash is placed in a small beaker or an evaporating dish and dissolved in the sodium hydroxide solution from the side-necked test-tube. Into it is run, drop by drop, a mixture of 90 parts of sirupy phosphoric acid and 10 parts of a solution of sulfurous acid (0.1 N or stronger and titrated recently). The addition of acid is continued until effervescence ceases. The solution is then boiled for about five minutes to expel the sulfur dioxide. It is tested with indicator paper (made by evaporating an alcoholic solution of brom phenol blue on ash-free filter paper) by removing a small drop on a glass needle and touching it to the paper. If the indicator paper does not change quickly from blue to yellow, concentrated sulfuric acid should be added drop by drop until it does change the paper as indicated.

This solution is now run into a 12-cc. separatory funnel which has an etched mark at a volume of 10 cc. and made up to the mark with distilled water. A small crystal (about 1 mg.) of sodium nitrite is added, the stopper inserted and the nitrite dissolved by agitation. One cc. of purified carbon tetrachloride (see first paper) is introduced into the separatory funnel, gently agitated or inverted 200 times so as to bring about partition-equilibrium between the iodine in the water and the carbon tetrachloride. If the carbon tetrachloride is at all cloudy, it is run into a 1 cc. centrifuge tube and centrifuged until clear. It is then placed in the left cup of a Bausch and Lomb micro-colorimeter and set at 20 mm. In the right cup of the colorimeter is placed about 1 cc.

of carbon tetrachloride containing 0.1 mg. of iodine per cc. and a color match made. An average of ten readings on the right side in mm. divided by 20 and multiplied by 0.1 (the concentration of the standard) gives the milligrams of iodine in the carbon tetrachloride, and this multiplied by 1.118 gives the milligrams of iodine in the sample analyzed. As a check on the extraction, 0.1 cc. of the water in the separatory funnel is run into a small vial containing a minute crystal of potassium iodide. A drop of carbon tetrachloride is added and the vial agitated. If the carbon tetrachloride does not become pink, a drop of conc. sulfuric acid is added to the separatory funnel and the process is repeated. If the pink color appears this time, 1 cc. of carbon tetrachloride is added to the separatory funnel, the extraction and reading are made and the yield is added to that of the first extraction.

At the end of the combustion it will be found that some ash has adhered to the silica. This is only enough to cause a slight error in the analysis but is sufficient to shorten the life of the silica tube, due to the difference in expansion of silica and ash. The life of the tube may be prolonged by rubbing off as much of the ash as possible with sand paper and then dissolving the remainder first with hydrochloric and then with hydrofluoric acid before heating the tube again. If the tube cracks off at the end it may be cut off or used for burning oils (to be described in the third paper). An elbow made by bending the silica tube is much less liable to break than an elbow that is fused on. Hence the larger tubes described in the first paper are not economical.

If the vegetables contain much chloride the wires in the Cottrell precipitator must be sealed in glass tubes run through the rubber stoppers in order to preserve the insulation.

The percentage of the total iodine caught by the Cottrell precipitator varies with the nature of the vegetable that is burned. If this percentage is determined for one sample of vegetable and found to be low it may be desirable to omit the Cottrell precipitator in analyzing similar samples, its place being taken by 4 or more Milligan wash bottles connected in parallel and a tube of 25 mm. bore 500 mm. long packed with moist glass wool. If no soot is formed the smoke is largely alkali chlorides.

In the second combustion (in the pyrex combustion tube) the material is alkaline and only a small percentage of iodine is volatilized and caught in the side-necked test-tube. This method of combustion is almost as convenient as combustion in an open crucible, however, and since some form of furnace is necessary to prevent overheating of the crucible, the pyrex tube forms a convenient type of furnace as regards visibility. If the ash fuses it may be necessary to add potassium nitrate to it for complete combustion, in which case the liability of loss of iodine from an open crucible is increased.

Some chemists have had difficulty with the method due to the material to be burned adhering to the open end of the steel tube. This is due to the tube becoming too hot or the material being in powdered form. The steel tube should not be inserted *inside* of a silica tube in which the combustion takes place. If the material is not made into sticks it may be burned in a sheet iron "boat" about 6 inches long with a handle or empty portion 18 inches long. About 30 g. of the ground vegetable or vegetable compressed into tablets is spread over the bottom of the boat, ignited and burned. The boat is withdrawn and another 30 g. added and the process repeated until the whole is burned. Since a similar method was described in the first paper, no special details are added here except to suggest that the silica tube herein described is more economical than the larger one described in the first paper. In using the boat an oxygen inlet tube may be held up by an independent support and inserted into the silica tube as far as the most advanced end of the boat so that combustion begins at this end first and only gradually spreads over the material in the boat. The use of the boat is very unsatisfactory if the vegetable has a high fat content.

Extraction of Ash Containing Large Quantities of Soluble Salts.—The ash is extracted repeatedly in a ball mill with 95% alcohol (recently distilled over sodium hydroxide), or enough alcohol to cover the ash is added, and allowed to stand for fifteen minutes with occasional gentle stirring with a glass rod. The alcohol is decanted through a small ashless filter, the residue being retained in the dish. A second portion of alcohol is now added, and the residue rubbed with a small porcelain pestle. The ash contains considerable alkali carbonates, which extract water from the alcohol, forming a 3-phase system and the mass is at first gummy and adheres to the pestle, but later becomes pasty, so that trituration with the alcohol becomes easy. The residue is washed with a third portion of alcohol, triturating it thoroughly, and the alcohol is passed through the same filter as before.

TABLE I

ANALYSES BY THE METHOD

Potassium iodide was added to 50 g. of iodine-free starch with the following results:

Added	0.200 mg.	Found by analysis	0.194 mg.

Iodine in Vegetables from South Carolina

	Field peas	Okra	Potatoes	Sweet potatoes	Peaches
Dry matter, %	90.6	8.9	19.7	31.0	11.1
I_2, dry basis, parts per billion	197	412	333	115	192

California Vegetables

	Asparagus	Beets	Carrots	Celery	Peas	Spinach	Tomato
I_2, dry basis, parts per billion	12.0	8.0	8.0	14.0	9.0	32.0	20.0

Alternative Method Using Low-Temperature Ashing.—If the sample is of cereal grain (which gives an acid ash), it should be moistened with 50 cc. of 2% calcium lactate solution followed by 50 cc. of 2% sodium carbonate solution. The sample is dried, coarsely ground and heated in an evaporating dish over a small flame until the vegetable matter begins to smolder. The heat is now withdrawn so that the sample will continue to smolder and burn at low temperature, without flame. If smoldering ceases the dish may be heated again until ignited.

After this preliminary ignition, during which the sample will be completely converted into a black char, the dish is placed in a muffle and maintained at a temperature which must not exceed 450° until ashing is practically complete and the ash is light gray in color. It is not usually practicable to carry the ignition to complete whiteness of ash. This ignition in the muffle will require from twelve to fifteen hours.

TABLE II

ANALYSES BY THE LOW-TEMPERATURE METHOD

Sodium iodide was added to half of a sample of dried, ground potatoes and not to the other half and the halves were analyzed separately, with the following results:

Dry sample	Iodine, mg.
100 g. of potatoes—0.1 mg. of iodine	0.129
100 g. of potatoes	.034
Added iodine recovered	0.095 = 95%

South Carolina potatoes	Sample 1	Sample 2	Sample 3
I_2, parts per billion	338	348	369

Summary

A method has been described for the rapid combustion of vegetables for iodine analysis which necessitates the use of oxygen and special stoking to prevent soot and tar formation and results in volatilization of chlorides and iodides. These are not all caught by ordinary wash bottles. A simple form of Cottrell precipitator will precipitate all the smoke (largely alkali chlorides) provided it is large enough for the rest of the apparatus. The precipitator and mechanical stoking apparatus are shown in Fig. 1.

Low-temperature burning in open dishes requires about fifteen hours for 100-g. dry samples and does not result in large losses of iodides if the ash is alkaline and temperature never above 450°. Combustion is never complete if the ash fuses. Calcium lactate must be added to vegetables with an acid ash (cereals) in order to make the ash alkaline and prevent fusion of the ash.

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