Taylor, from Dr. Hans L. J. Bäckström and from Dr. R. N. Pease. We should also like to state that we are indebted to a Procter Visiting Fellowship at Princeton for assistance in carrying out this work.

Summary

The thermal oxidations of benzaldehyde and formaldehyde in the vapor phase have been investigated. It has been shown that they are both chain reactions, judged by the characteristic suppression of the rate of oxidation when it is carried out in a packed vessel. The mechanism of the benzaldehyde oxidation is discussed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTH CAROLINA FOOD RESEARCH COMMISSION AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

THE DETERMINATION OF TRACES OF IODINE. IV. IODINE IN SMALL QUANTITIES OF THYROID AND OTHER TISSUES[1]

BY ROE E. REMINGTON, J. F. McCLENDON, HARRY VON KOLNITZ AND F. BARTOW CULP

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The tube furnace method originated by one of us[2] for the destruction of organic matter in the estimation of traces of iodine has been modified and adapted to the analysis of thyroid and other glands, oysters and other animal tissues relatively high in iodine. It possesses advantages of brevity and accuracy which make it preferable to any other method which has been described. Other workers have destroyed organic matter in thyroid by fusion with sodium hydroxide, or with sodium hydroxide and potassium nitrate[3] or a carbonate mixture. It has also been done by digestion with sulfuric acid and hydrogen peroxide.[4] All of these processes are time consuming and open to the possibility of loss.

We have found[5] that vegetables can be ignited in a muffle at 450° or less without material loss of iodine but if the temperature is raised to 550° the results are usually low. On dried thyroids, alone or with the addition of calcium oxide or sodium hydroxide, the low-temperature method is not satisfactory. If 0.1 g. of dried thyroid is mixed with 100 g. of dried potatoes, the iodine can be recovered with a fair degree of accuracy, but requires from twelve to twenty-four hours in the muffle and previous careful analysis of the potatoes.

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[1] Presented before the Division of Biological Chemistry at the 78th meeting of the American Chemical Society, Minneapolis, Minnesota, September 9–13, 1929.

[2] J. F. McClendon, THIS JOURNAL, **50**, 1093 (1928).

[3] E. C. Kendall, *J. Biol. Chem.*, **43**, 149 (1920).

[4] G. Pfeiffer, *Biochem. Z.*, **195**, 128 (1928); E. Glimm and J. Isenbruch, *ibid.*, **207**, 368 (1929).

[5] J. F. McClendon and R. E. Remington, THIS JOURNAL, **51**, 395 (1929).

When we tried to burn powdered thyroid in the tube furnace with the original technique of heat under the tube, most of the material underwent dry distillation. We then tried heating the material by means of a miniature oxygen–gas torch made by soldering together two ordinary laboratory blowpipes. On the powder alone this also caused too rapid burning, and the appearance of tarry matter in the absorption bottles. We next tried diluting the thyroid powder with an excess of inert material, using for this purpose calcium oxide, sodium hydroxide, calcium carbonate, sodium carbonate and sand. Calcium oxide was found most satisfactory if fat had been previously extracted from the thyroid, but if any fat is present, traces of fatty acids may distil onto the sides of the tube and by their effect on surface tension interfere later with the removal of the lime by centrifuging. Acid-washed and ignited sand is very satisfactory for such samples. The subsequent treatment of the ash residue and liquids from the absorption jars is the same as previously described, except that a small amount of sodium azide is used as recommended by Reith,[6] to reduce any nitrites which may be produced in the burning of protein in oxygen. It was found that the iodine from 0.01 g. of thyroid powder could be determined easily colorimetrically when shaken out in 1 cc. of carbon tetrachloride. (The lower limit of accuracy with the Bausch and Lomb micro-colorimeter is probably about 0.01 milligram of iodine for most observers. This amount is contained in 5 milligrams of thyroid powder of 0.2% iodine content.) However, when abundance of material is at hand, greater accuracy in sampling and weighing is obtained by using 0.1 to 0.2 g. of the powder and shaking out the iodine from one-fifth of the final solution. The size of the combustion apparatus has been very much reduced and side-neck test-tubes substituted for the various wash bottles of the original set-up. The combustion can be completed in about five minutes, using a Richards or other water-operated suction pump, and the washing up of the apparatus does not take more than ten minutes. The complete set-up (Fig. 1) is as follows.

The pyrex combustion tube is 210 mm. long and of 25 mm. bore, with a right-angled outlet tube 155 mm. long and of 5 mm. bore. The outlet leads into a side-neck pyrex test-tube 150 mm. long and of 15 mm. bore. From the side neck a rubber connection joins the tube with two test-tubes set in parallel by means of a Y-tube. These test-tubes are fitted as gas wash bottles with 3-mm. bore tubing, the inlet tubes being drawn into capillaries. The gas stream is united again by another Y-tube and leads into the bottom of a large soda lime tube 235 mm. high and of 20 mm. bore, set vertically. This tube has a small porcelain filter disk in the bottom of the bulb and is nearly filled with fine glass wool. A tube from the top leading to a suction flask connected with a suction pump completes the set-up. The three test-tube wash bottles are filled and the glass wool is moistened with a very weak solution of sodium sulfite. The wash bottles

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[6] J. F. Reith, "De Micro-Jodiumbepaling in Natuurlijka Grondstoffen," Dissertation, University of Utrecht, 1929.

are immersed in ice water. There is a screw clamp set on the rubber connection below the tower which is used to regulate the suction and to keep the solution in the tower from flowing back into the wash bottles. The two blowpipes forming the torch are soldered together at their centers and the tips may be filed slightly on the inside so as to bring them nearer together. (Hoke, Incorporated, have recently made for us a miniature oxygen–gas torch with a special outlet tube, which is very satisfactory.) The bent end is only about 1 cm. long, so as to give the maximum clearance. Ordinary illuminating gas is used in the lower pipe while oxygen is used in the upper. The combustion boat is of nickel, one end being cut away to admit the torch. It is about 1.5–2.0 cm. wide, 4.0–5.0 cm. long and 1 cm. deep.

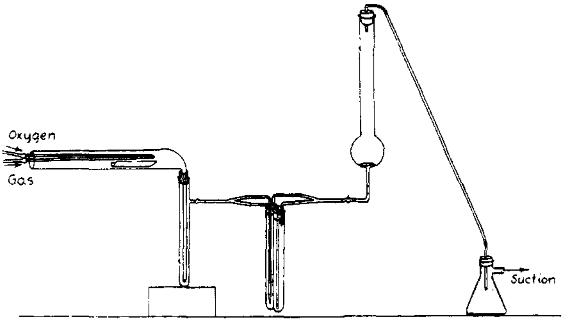

Fig. 1.

Manipulation

The fresh thyroids are weighed, cut into bits and dried at 100° for 24 hours for a rough moisture determination. The resulting glassy mass is ground and a second moisture determination made. Fat is then extracted with anhydrous ether in a Bailey–Walker apparatus.

Approximately 0.1 g. of the powder is accurately weighed into the nickel boat, mixed with about twice its volume of freshly ignited calcium oxide, by means of a platinum wire, and finally covered with a thin layer of the lime, so that no thyroid material can be seen on top. The boat is inserted into the combustion tube until it is about 4 cm. from the inner end of the tube, and the suction regulated by the screw clamp until there is a steady flow which does not draw any solution into the next receiver.

The torch should be so adjusted that the flame will be non-luminous throughout and yet of a force insufficient to blow any material from the boat. An excess of oxygen is used. The sample should be burned slowly, manipulating the torch by hand, starting at the far end of the boat and working toward the rear. (A pair of smoked glasses will be a very great help in watching the combustion.) After the first burning, the mass is stirred or turned over with a platinum wire, so as to expose and re-burn any black spots which remain. This may be repeated if there is further black residue. The entire burning can be completed in five minutes, and the solutions in the absorbers should be perfectly clear and colorless.

The receivers and combustion tube are rinsed into a 250-cc. beaker and the boat with its residue is placed in the beaker. The tube can be more easily washed if some alcohol is used first. The washing of the tower is easily done by connecting the suction flask to the lower outlet and washing the glass wool by gentle suction. The contents and washings of the entire apparatus should not exceed 225 cc.

This volume is evaporated down to about 50 cc., centrifuged from insoluble lime and evaporated to small volume. It is then transferred to a nickel or platinum boat and the evaporation continued to complete dryness. About 0.5 g. of powdered sodium hydroxide is sprinkled over the residue, the boat placed in a combustion tube like the one formerly used and heated by a flame beneath the tube until the hydroxide is completely fused; meanwhile a slow current of air is drawn through the tube and a single absorption tube. This method of fusing with alkali is no more troublesome than fusion in an open dish, and avoids the dangers of overheating and loss of iodine.

The flux is allowed to cool, dissolved in a small amount of water and transferred with the liquid from the absorber and the rinsings of the tube to a 50-cc. beaker. A few mg. of sodium azide is added, the solution made just acid to brom phenol blue paper with sirupy phosphoric acid and 5–10 drops added in excess followed by 5 drops of 8% sulfurous acid. The indicator paper must not be dipped into the solution, but a tiny drop removed on a small rod for the test. It is then heated until the odor of hydrazoic acid disappears, cooled, transferred to a 50-cc. volumetric flask, made to mark and 10 cc. removed to a small separatory funnel for the colorimetric estimation of iodine as previously described.[2]

TABLE I

ANALYTICAL RESULTS

	Weight taken, g.	Iodine recovered, %		Weight taken, g.	Iodine recovered, %
Thyroid powder	0.0925	0.181	Anterior pituitary	0.1589	0.0149
(U. S. P. Lilly)	.4325	.185	(Armour)	.1906	.0126
	.1225	.185		.1914	.0134
	.1232	.179		.2056	.0135
	.1105	.188		.2269	.0130
	.1695	.182			———
	.0897	.186		Av.	.0135
	———	———	Salamander thyroids[a]		
	Av.	.184	(dry weight)	.0262	.342
Oysters, dry basis,	.8540	.00162	Salamander back		
Charleston Co., S. C.	.7772	.00154	muscle[a] (dry weight)	.0618	.0068

[a] We are indebted to Dr. E. Uhlenhuth of the University of Maryland for the salamander tissues.

TABLE II

HUMAN THYROIDS[a] FROM CHARLESTON, SOUTH CAROLINA

No.	Sex	Age	Weight of entire gland, g.	Cause of death	Iodine in dry fat-free material, %	Iodine in total gland, mg.
8557	F	35	15	Pellagra	0.153	6.66
8598	F	2.5	6	Malaria	.083	0.73
8604	M	26	13	Head injury	.202	7.12
8619	M	38	16	Syphilitic ulcer of duodenum and obstruction	.295	12.90
8628	M	38	14	Myelogenous leukemia	.160	4.75
8633	M	50	35	General arteriosclerosis	.101	6.34
8635	F	50	13	Syphilitic encephalitis	.264	8.84
8669	M	14	10	Suppurative appendicitis and peritonitis	.069	1.63
8670	M	65	12	Acute purulent meningitis	.192	5.54
8672	F	..	16	Suppurative appendicitis and peritonitis	.123	4.53
8686	M	78	10	General arteriosclerosis	.280	6.01
8706	F	16	13	Acute suppurative pyelo-nephritis	.333	10.07
8719	F	38	..	Stab wound of chest	.200	....

TABLE II (*Concluded*)

No.	Sex	Age	Weight of entire gland, g.	Cause of death	Iodine in dry fat-free material, %	Iodine in total gland, mg.
8732	M	32	14	Arterio-capillary sclerosis	.594	23.70
8733	M	28	16	Not definitely determined	.201	6.75
8745	F	35	..	Arterio-capillary fibrosis	.327	10.00
8757	M	28	11	Intestinal obstruction	.229	6.24
8762	..	..	1.5	New-born	.061	0.22
8769	F	30	18	Arterio-capillary sclerosis	.447	19.2
8787	M	33	16	Syphilitic hemorrhagic pachy-meningitis	.203	7.89
8800	F	70	15	General arteriosclerosis	.167	5.12
8820	M	17	20	Stab wound and hemorrhage	.304	20.9
8865	..	..	1.5	Infant	.070	0.195
8888	..	..	1.8	Infant	.020	0.065
8894	..	2	2	Tuberculosis	.109	0.423
8898	M	70	15.5	Pulmonary tuberculosis	.275	9.70
8910	..	..	2	Infant	.026	0.118
8916	M	55	26	Syphilitic encephalitis	.163	11.15
8922	F	26	13	Stab wound of chest and heart	.133	3.67
8941	F	30	16	Acute suppurative pyelo-nephritis	.135	4.33
8942	M	32	19	Gun shot wound, abdomen and peritonitis	.210	8.36
8961	F	50	13	Diabetes mellitus	.172	4.95
9058	F	50	21	Lobar pneumonia	.194	7.81
9076	M	35	17	Peritonitis	.259	10.65
9245	F	38	19.1	Not clearly determined	.233	11.67
9256	M	47	14.5	Not determined	.280	6.92
9260	M	27	17.5	Cardiac failure	.087	2.49

[a] We are indebted to Drs. Kenneth M. Lynch and H. H. Plowden of the Department of Pathology, Medical College of the State of South Carolina, for the material and pathological data.

If the quantity of iodine is low, or it is desired to use smaller samples, the entire solution may be boiled down to 5–8 cc. before acidifying, all transferred to the separatory funnel and made up to 10 cc. We have been able to determine iodine in 50 mg. of fresh salamander thyroid, in 0.15 g. of dried anterior pituitary and in 0.75 g. of dried oysters by this method. A sample of desiccated thyroid examined by Kendall's method gave duplicate values of 0.182 and 0.186%, after correcting for blank tests on the reagents. Seven determinations by our method gave values ranging from 0.179 to 0.188% with an average of 0.184. Some typical results are given in Table I. Results on 37 human thyroids from a non-goitrous region (Charleston, S. C.), are given in Table II.

Summary

A micro-modification of the McClendon tube furnace method for iodine estimation has been developed which is applicable to small quantities of biological materials such as thyroid and other glands oysters and other sea food. Aside from the reduced size of the apparatus, the essential

modifications are the use of an oxygen-gas torch to burn the sample and the use of lime to retard the combustion and alkalinize the ash. Results are given on thyroid, pituitary, oysters and a series of 37 human thyroids.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 244]

THE EQUILIBRIUM BETWEEN BIVALENT AND QUADRIVALENT PALLADIUM AND CHLORINE IN HYDROCHLORIC ACID SOLUTION

BY HOMER B. WELLMAN

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Introduction

The equilibrium between palladous and palladic chlorides and chlorine in hydrochloric acid solution seems not to have been previously measured, and no physico-chemical studies have been made as to the state in which bivalent and quadrivalent palladium exist in chloride solutions. It is well known, however, that from such solutions salts of the types R_2PdCl_4 and R_2PdCl_6 separate, and it is probable that in such solutions the palladium exists mainly or wholly in the form of the corresponding ions $PdCl_4^{--}$ and $PdCl_6^{--}$. In that case the equilibrium to be here considered would be expressed by the simple equation: $PdCl_4^{--} + Cl_2 = PdCl_6^{--}$.

It was necessary, however, to consider the possible existence of trivalent palladium in the solution, for complex salts of this valence have been prepared.[1] Therefore, it was thought advisable in some of the experiments to fix the concentration of quadrivalent palladium by saturating the solutions with the slightly soluble potassium chloropalladate (K_2PdCl_6), and to estimate the concentration of trivalent palladium in these solutions by determining the total oxidizing chlorine. Accordingly, one of the steps in this investigation consisted in determining the solubility of potassium chloropalladate. Solutions of palladous chloride in normal hydrochloric acid containing known amounts of potassium chloride were saturated with chlorine at atmospheric pressure, whereby all of the palladium is oxidized to the quadrivalent state. The solubilities of potassium

[1] Wöhler and Martin, *Z. anorg. Chem.*, **57**, 398–413 (1907), by treating the hydrochloric acid solution of palladous chloride with cesium and rubidium chlorides and chlorine, prepared the compounds Cs_2PdCl_5 and Rb_2PdCl_5, which they found to be more unstable than the corresponding quadrivalent compounds. They failed to prepare K_2PdCl_5 by this method, but with considerable difficulty they obtained some of this compound by treating the oxide, Pd_2O_3 (formed at the anode in electrolyzing palladous nitrate), with potassium chloride and dry hydrogen chloride in ether.