possible to calculate the thermionic-work functions, and hence contact potentials between metals, from thermoelectric data.

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Received February 20, 1923

[Contribution from the Dermatological Research Laboratories]

QUANTITATIVE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS WITH ARSENIC AND WITH MERCURY

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Received May 22, 1922

Analysis of Arsenical Compounds

During the past 20 years, the method for the quantitative analysis of carbon and hydrogen in organic compounds has been both greatly simplified and improved through the introduction by M. Dennstedt of a new method to combustion in a current of oxygen, with platinum as a catalyst. With regard to the saving of time and energy, this method is superior to any other, and yields results as accurate as those obtained by the older Liebig method. The procedure has been further developed so that in organic substances containing nitrogen, sulfur and halogens these elements may be determined simultaneously with carbon and hydrogen. Organic arsenicals or mercurials, however, could not be analyzed in this way, because of "poisoning" of the platinum catalyst by the arsenic oxide or mercury vapors formed. As the authors have been engaged in the preparation of organic compounds containing these elements, it was considered essential to obviate the above difficulty. Not only has this been accomplished, but in addition, the method developed for the concurrent determination of mercury appears to be superior to the usual gravimetric method, in so far as accuracy and rapidity are concerned.

In order to prevent arsenic oxide from attacking the platinum, a boat B containing red lead is placed immediately after the boat A containing the substance to be analyzed (Fig. 1). The red lead reacts quantitatively with arsenic oxide, forming lead arsenate which does not decompose at high temperatures. If the combustion is not conducted too rapidly, the lead arsenate may be observed as a thin white coating at that end of the boat B nearest A, except in the case of sodium salts containing sufficient sodium to combine with all of the arsenic when no such coating is formed. The stability of the lead arsenate at high temperatures is of great convenience as carbonaceous matter, which frequently settles upon it, can be entirely removed by continued heating.

Both the apparatus and the procedure are identical with those described by Dennstedt,[1] except that the wider part of the inner tube is 5 or 6 cm. longer, and that Boat B containing red lead is placed 3 cm. from Boat A.

The red lead is prepared from pure lead peroxide, by drying in an oven at 140° and then gradually heating it in a current of oxygen until it is dark red, after which it is cooled and kept in a desiccator. After each analysis it is merely necessary to remove any coating of lead arsenate formed, and replace it with fresh reagent. For substances containing about 35% of arsenic, Boat B should be about 8 cm. long, and for those with higher arsenic content, from 10 to 11 cm. long. At the beginning of the analysis, the portion of red lead nearest the catalyst is heated with an ordinary Bunsen burner, and as the combustion progresses, the flame is gradually moved toward the other end of the boat.

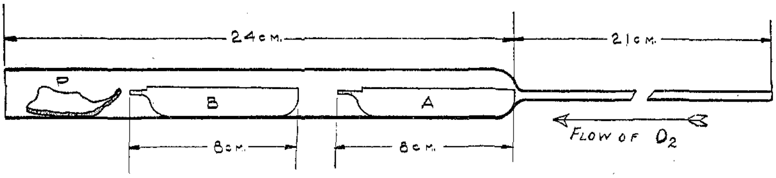

Fig. 1.—Inner tubes for analysis of organic arsenicals.

A, porcelain boat with substance; B, porcelain boat with red lead; P, a piece of broken porcelain to prevent the accidental deposition of any particles upon the catalyst.

The authors have performed a great number of analyses of organic subtances containing arsenic, and have rarely met with an accident in which the platinum was " poisoned." Should this occur, it may be revivified by boiling for about 3 hours in 20% nitric acid, washing with hot water and drying. The analysis usually proceeds smoothly, and requires a maximum time of 2 hours. In working with explosive compounds,

Table I

Analytical Results for Carbon and Hydrogen

Compound	Carbon Calc. %	Carbon Found %	Hydrogen Calc. %	Hydrogen Found %	Remarks
3 - Nitro - 4 - hydroxyphenylarsonic acid	27.37	27.17	2.28	2.54	Calc.: As, 28.57; N, 5.32. Found: As, 28.45 (Lehman); N, 5.36 (Kjeldahl)
Commercial sample of arsphenamine	[a]	28.9	[a]	4.1	
		28.9	..	3.9	
p - Aminophenyl arsonic acid (*p*-arsanilic acid)	33.17	32.97	3.68	4.0	

[a] Since it has not as yet been definitely established whether commercial arsphenamine contains 2 H_2O or 1 CH_3OH "of crystallization," the theoretical figures for carbon and hydrogen are omitted.

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[1] Dennstedt, "Anleitung zur Vereinfachten Elementaranalyse," Otto Meissners, Hamburg, 4th ed., **1919.**

such as those containing nitro groups, etc., the substance is mixed with sea sand and analyzed according to Dennstedt.[2] Otherwise, some of the red lead may be blown upon the catalyst, rendering it useless for further analysis.

The preceding table shows the results obtained for carbon and hydrogen in various organic arsenicals according to the modification described.

Mercurial Compounds

For the analysis of organic mercury compounds, the time required is somewhat longer than in the case of arsenicals, the combustion alone requiring from 45 to 60 minutes and the entire analysis, from 2 to 2.5 hours. The development of the following procedure is the result of our observations that silverized asbestos is capable of quantitative amalgamation with metallic mercury, and that the amalgam formed is unaffected by *oxygen at comparatively high temperatures. To prevent any carbon*aceous matter from depositing upon the silverized asbestos in E, a small boat D almost filled with a mixture of red lead and sea sand is inserted between the latter and the compound analyzed in C, Fig. 2. In our analyses thus far, the platinum has never been affected by mercury, except with explosive substances. Should "poisoning" occur, the catalyst may be revivified as previously indicated.

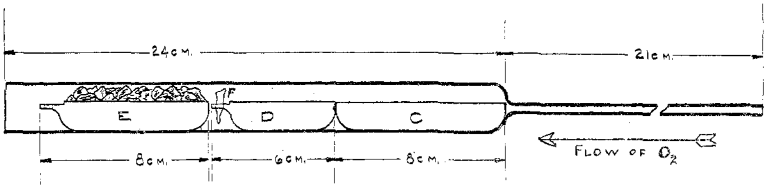

Fig. 2.—Inner tube for analysis of organic mercurials.

C, porcelain boat with substance; D, porcelain boat with red lead and sea sand mixture; E, porcelain boat with silverized asbestos; F, piece of broken porcelain.

The general arrangement of the entire apparatus is the same as described by Dennstedt, except that the wider portion of the inner tube (Fig. 2) is 24 cm. long, and that two additional boats, D and E, are required. It is preferable that C be a boat without a handle so that D may actually touch it. As a further precaution against the entrance of any red lead particles into E, a piece of broken porcelain F is inserted into the handle of D.

Preparation of Silverized Asbestos.—The highest grade of asbestos is purified according to Treadwell,[3] thoroughly mixed with a solution of silver nitrate (90 g. per 100 cc.), and evaporated to dryness on a sand-bath. It is then broken into pieces about the size of a pea, and gradually heated to redness in a porcelain crucible, thereby com-

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[2] Ref. 1, p. 83.

[3] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, **1919**, vol. II, p. 26.

pletely reducing the silver nitrate to the metallic condition. The substance is then preserved over fresh calcium chloride.

In order to insure quantitative absorption of the metallic mercury E should be so filled with granules of silverized asbestos that when it is inserted in place in the inner tube, the space directly above it is almost entirely occupied (Fig. 2). Care must also be taken that none of the asbestos touches the walls of the inner tube so that E may be moved in and out of it without loss of material.

Mixture of Sea Sand and Red Lead.—A sample of commercial "Washed and Ignited Sea Sand" is thoroughly mixed with 2 parts of red lead prepared according to the method already described, and preserved over calcium chloride. The admixture of sea sand is necessary, as otherwise the vapors evolved from the mercury compound produce an explosion in D, scattering its contents throughout the inner tube.

Procedure.—The substance to be analyzed is placed in the rear (left) half of C so that the part of the boat nearest the capillary of the inner tube is entirely unoccupied, thereby eliminating the possibility of any mercury vapor entering the capillary. The combustion is conducted according to Dennstedt, excepting that the edge of the cover above the platinum does not lie in the same vertical plane with the end of the inner tube, but is placed about 1 cm. after it (to the left) to prevent overheating of the silver amalgam formed, and that the flame under the platinum is not moved during the entire combustion, but remains stationary so as to maintain a uniform temperature.

At the beginning of the analysis a large flame is placed at the extreme right of the combustion tube, as far as possible from the substance in C, while a very small flame is placed directly under the right end of D. The larger flame is maintained until the substance is practically entirely carbonized, when drops of metallic mercury become visible above C. It is then gradually moved to the left, a small cover placed above C, and the flame under D turned off. When all of the carbon has been oxidized, heating the catalyst is discontinued, and the flame under C placed at the extreme right end of D to assist in the oxidation of any organic matter which may have collected there. When this is completed almost all of the mercury has amalgamated with the silver in E, the remainder adhering to that part of the inner tube above the far (left) end of D. It should be noted that the large flame never extends beyond the center of D in order to avoid any volatilization of the mercury in E. All the flames are now turned off, and the apparatus is cooled in a stream of oxygen for about 20 minutes. The absorption tubes are then detached, and in order to amalgamate the last traces of mercury mentioned above, the inner tube is removed without interrupting the current of oxygen, E separated from D by a distance of about 2 cm. and the tube reinserted in its original place. A small cover is placed above C, and a large flame underneath it, while the far (left) end of D is heated by a small flame which is gradually moved toward E, until the mercury is completely amalgamated. This requires about 20 minutes. Should any of the mercury condense on the outer surface of the front (right) end of E, it can be driven into the silverized asbestos by gentle warming. The apparatus is cooled as before, E removed to a desiccator containing calcium chloride, and finally weighed.

The increase in weight represents the amount of mercury found in the substance. That the silverized asbestos remains unaffected by any of the volatile oxides formed during the combustion has been proved by the fact that it did not change in weight after analyses of both urea and sulfanilic acid.

The same sample of sand and red lead mixture can be used repeatedly if any white deposit formed on the surface is removed, and replaced with some of the fresh mixture. Similarly, it is unnecessary to recharge E with fresh silverized asbestos after each analysis, as it can be revivified without the possibility of the operator inhaling any mercury fumes by proceeding in the following manner: the boat containing the amalgam is placed in the center of a hard glass tube about 50 cm. long, 17 mm. in diameter and sealed at one end, while a second boat about 13 cm. long and containing silverized asbestos, is placed within a few centimeters of the open end of the tube. After the amalgam has been strongly heated for about 1.5 hours, the mercury is almost completely driven off, a part being retained by the silver in the larger boat, while the remainder condenses in the closed end of the tube. It is not necessary to ascertain whether or not the last traces of mercury have been removed, as the recovered silverized asbestos in E has a sufficient surface to combine with the mercury contained in the sample analyzed.

The following figures indicate that the combustion method for the determination of mercury in organic compounds yields results equally satisfactory to those obtained gravimetrically: by combustion: Hg, 65.91, 65.84%; by gravimetric analyses: 65.77%.

In Table II are shown the closely checking results obtained for carbon, hydrogen and mercury in 3 different organic mercurials analyzed according to the method described.

TABLE II

ANALYTICAL RESULTS FOR MERCURY, CARBON AND HYDROGEN

	Hg %	C %	H %
I	64.49	19.11	1.58
	64.56	19.22	1.64
II	65.96	18.00	1.76
	66.07	18.19	1.73
III	65.12	19.04	1.79
	65.14	19.20	1.76

Summary

1. A method has been described for the analysis of carbon and hydrogen in organic compounds containing arsenic.

2. A method has been described for determining carbon, hydrogen and mercury in organic compounds of mercury.

3. A comparison of the results for mercury obtained gravimetrically and by the combustion method indicates the superiority of the latter with regard to both speed and accuracy.

PHILADELPHIA, PENNSYLVANIA

THE PHYSICAL PROPERTIES OF MALEIC, FUMARIC AND MALIC ACIDS

BY JOHN MORRIS WEISS AND CHARLES R. DOWNS

Received August 4, 1922

The authors[1,2] have described the production of maleic and fumaric acids and the conversion of these acids into *i*-malic acid. Very little of any of these materials has in the past been available to investigators. In our work on these acids we have thoroughly searched the literature for physical properties, and some of the constants which are lacking have been determined under our direction. Much, however, remains to be done and now that the various materials are available in quantity to any investigator, we feel that the presentation of these results, incomplete though they are, will serve to stimulate further investigations in this field.

Melting Points

A careful series of tests indicated a value of 52.6° corrected for maleic anhydride. This is in very good accordance with results found by Anschütz,[3] Volhard[4] and Ossipoff,[5] who obtained results of 53°, 53° and 52°, respectively, but quite different from those of Dorn[6] and Tanatar[7] who obtained much higher results.

Pure *i*-malic acid melts sharply in both open and sealed capillary tubes at 128.5° to 129°. When the capillary was allowed to cool and then reheated, a value of 117° was obtained. A third repetition gave a figure of 114°. The length of time the capillary is held at the elevated temperature affects the melting-point lowering, which is due to the formation of malo-malic acid. Although the first reduction of melting point from 128.5° to 117° was greater than the second lowering, that is, from 117° to 114°,

[1] Weiss and Downs, *J. Ind. Eng. Chem.*, **12,** 228 (1920).

[2] Weiss and Downs, THIS JOURNAL, **44,** 1118 (1922).

[3] Anschütz, *Ber.*, **12,** 2280 (1879).

[4] Volhard, *Ann.*, **268,** 255 (1892).

[5] Ossipoff, *Compt. rend.*, **109,** 311 (1889).

[6] Dorn, *Ann.*, **188,** 87 (1877).

[7] Tanatar, *ibid.*, **273,** 32 (1893).