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THE DETERMINATION OF TRACES OF MERCURY. I. THE SENSITIVITY OF THE QUALITATIVE TESTS FOR MERCURY. A NEW METHOD FOR THE DETECTION OF MERCURY SENSITIVE TO ONE PART IN A BILLION[1,2]

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The efficacy of mercurial medication depends to a very large degree on the concentration of mercury in the body, and this in turn depends upon the balance between absorption and excretion. Reliable methods for the determination of small amounts of mercury in physiological fluids are, therefore, of great importance in the study of mercurial medication. Three principal sources of error in the methods which have been applied to urine and feces to which experimenters upon this subject have paid too little attention are (1) the qualitative test by which the accuracy of the quantitative work is controlled; (2) the volatility of mercury salts; (3) the hydrolysis of mercury salts.

None of the previously published methods makes mention of the sensitivity of the qualitative test used to control the quantitative method, and in many cases the tests employed were found by us to be not sufficiently delicate to detect as small an amount of mercury as the quantitative method was intended to determine. Our first problem was, therefore,

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[1] This research has been carried on in collaboration with Dr. T. Sollmann, Dr. H. N. Cole and Dr. Karl G. Zwick of the School of Medicine of Western Reserve University, as a preliminary to a comprehensive study of the absorption and elimination of mercury and mercury compounds by the human body.

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[2] Presented at the Washington meeting of the American Chemical Society, April, 1924.

to make a careful study of the sensitivity of the qualitative tests for mercury, and if none was sufficiently sensitive, to evolve a new test to control the quantitative method.

Experimental Part

Solutions of mercuric nitrate containing the equivalent of 500, 50, 5 and 0.5 mg. of mercury per liter were prepared for studying the various tests.

Colorimetric Tests.—In each case 1 cc. of the solution of mercury salt was poured into a test-tube and a few drops of the test reagent were added. The concentration at which the reagent failed to give a characteristic reaction was noted (see Table I).

Hydrogen sulfide, stannous chloride, potassium iodide and ammonium thiocyanate are the reagents usually employed for detecting mercury salts. Ammonium thio-acetate and acetylene are also often recommended in textbooks of qualitative analysis. We found that the lower limit of sensitivity of these reagents was about 5 parts of mercuric ion per million. Hydrogen sulfide, stannous chloride, ammonium thiocyanate and acetylene showed a slight turbidity at this dilution, while in the case of potassium iodide and ammonium thio-acetate the results might be considered doubtful. Phenylthiohydantoic acid (which has been used[3] as a reagent for determining cobalt) and diphenylcarbazide[4] gave positive tests at a dilution of 5 parts of mercuric ion per million, but were not sensitive to 0.5 part per million. Mayer's reagent[5] was diluted to various concentrations, so that the mercury content was equivalent to 500, 50 and 5 mg. of mercury per liter, and the effect of these solutions tried on various alkaloids, such as brucine, caffeine and theobromine. Its limit of sensitivity was found to be 50 parts per million of mercuric ion. It is obvious that none of these reagents, which have always been considered as sufficiently sensitive, was delicate enough to be used as a control for a quantitative method.

Microscopic Tests.—One drop of each of the solutions of mercury salts described above was placed on a glass slide, one drop of the test reagent added, the mixture gently evaporated and then examined under the microscope to see whether any characteristic color or crystal growth could be observed. Of these tests, the reversal of the Nessler method,[6] the cupro-mercuric-iodide[7] and diphenylcarbazide tests were sensitive to 5 parts of mercuric ion per million, while the cobalt thiocyanate, potassium iodide and diphenylamine tests were sensitive to only 50 parts of mercuric ion per million. It is apparent that 5 parts of mercuric ion per million was

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[3] Willard and Hall, THIS JOURNAL, **44**, 2237 (1922).

[4] Cazeneuve, *Bull. soc. chim.*, [3] **23**, 701 (1900).

[5] Mayer, *Z. anal. Chem.*, **2**, 225 (1863).

[6] Moore, THIS JOURNAL, **33**, 1117 (1911).

[7] Artmann, *Z. anal. Chem.*, **60**, 81 (1921).

the greatest sensitivity that could be reached with the reagents tried by microqualitative methods.

Amalgamation Test.—As the amalgamation method has been considered very delicate, it was tried in the hope that it would have a greater sensitivity than 5 parts of mercuric ion per million. A drop of a mercury salt solution was placed on a glass slide and a small drop of nitric acid added. A short piece of highly polished, 36-gage (B. and S.) copper wire was laid in the solution and the reaction watched under the microscope. Bubbles of gas were first evolved, then the mercury began to be deposited and formed a silvery-white amalgam with the copper. This method was found to be sensitive to 5 parts of mercuric ion per million, but in such dilute solutions the reaction is slow and requires several hours before any mercury is apparent.

Electrolytic Test.—In order to speed the amalgamation test, and to concentrate the deposit of mercury, a small current of electricity was passed through the test drop, using the sharpened tip of a tiny copper wire as a cathode. This electrolytic test surpassed every expectation, both in rapidity and in sensitivity, and was adopted to control the quantitative process. The working details of this new method are as follows.

TABLE I

SENSITIVITY OF QUALITATIVE TESTS

Colorimetric test	500 mg. per l., using 1 cc. 500 p.p.m.	50 mg. per l., using 1 cc. 50 p.p.m.	5 mg. per l., using 1 cc. 5 p.p.m.	0.5 mg. per l., using 1 cc. 0.5 p.p.m.
Hydrogen sulfide	++	+	sl. turb.	−
Stannous chloride	++	+	sl. turb.	−
Potassium iodide	++	+	±	−
Ammonium thiocyanate	++	+	sl. turb.	−
Ammonium thio-acetate	++	+	±	−
Acetylene	++	+	sl. turb.	−
Phenylthiohydantoic acid	++	+	+	−
Diphenylcarbazide	++	+	+	−
Aniline	++	+	−	−
Tannic acid	++	+	−	−
Mayer's reagent for alkaloids	++	+	−	−
Microscopic test	Using 1 drop	Using 1 drop	Using 1 drop	Using 1 drop
Potassium iodide	++	+	−	−
Diphenylamine	++	+	−	−
Cobalt thiocyanate	++	+	−	−
Cupromercuric iodide	++	+	+	−
Reversal of Nessler reagent	++	+	+	−
Diphenylcarbazide	++	+	+	−
Amalgamation with copper	++	+	+	−
Electrolytic (our method)	+++	++	+	+

The electrolytic test (our method), after isothermal concentration at room temperature, is easily sensitive to 1 part in one billion parts of solution.

Significance of symbols: −, no reaction; ±, doubtful reaction; sl. turb., slight turbidity; +, definite reaction, precipitation or color; ++, marked reaction; +++, strongly marked reaction.

New Electromicroqualitative Method for the Detection of Minute Amounts of Mercury

A 36-gage (B. and S.) copper wire is highly polished with emery paper to a fine point and is cemented with de Khotinsky cement to a glass microscope slide with a central cavity (an ordinary "culture slide") in such a manner that the wire is firmly held with its free end sloping into the cavity. This serves as the cathode; a small platinum wire similarly mounted serves as an anode. These electrodes are connected to heavier wires and then to a source of current. If a permanent apparatus is desired, small binding posts can be cemented to the glass slide about 2.5 cm. from the center of the cavity. These will keep the electrodes firmly in position and also facilitate the removal of the copper wires. A drop of the solution to be tested is placed in the cavity on the slide and acidified with nitric acid. The platinum anode is set into the drop, but *only* the *tip* of the point of the copper cathode is allowed to touch it. A current of 1.3–1.5 milliamperes and of 1.5–2 volts is then passed through the drop. When the solution is not extremely dilute, two to three minutes is long enough for detection of the mercury. The circuit is then broken, the copper wire is removed, washed with water and examined under the microscope, or it may be examined during the progress of deposition. A silvery-white amalgam, turning greenish-yellow upon standing, shows the presence of mercury. By this method the mercury in one drop of a solution of mercury salt containing 0.5 mg. of mercury per liter can be detected; that is, a sensitivity of 1 part in two million. The sensitivity can be easily increased 1000-fold by evaporating 25–50 cc. of the test solution to a few drops in a vacuum desiccator over sulfuric acid. The residue is moistened with a drop of nitric acid, carefully stirred with a small, pointed glass rod to collect all the mercury salt into the drop, the drop then transferred to the glass slide and tested for mercury as described above. By using this preliminary concentration the electrolytic test is easily sensitive to one part per billion. In controlling our quantitative studies, 25 cc. of the solution was first concentrated by isothermal evaporation at room temperature to a volume of one drop and this drop tested electromicroscopically as described above, so as to give the sensitivity of one part per billion.

Summary

1. Most of the qualitative tests previously used failed at a dilution greater than 5 mg. of mercury per liter.

2. A new method for the qualitative detection of mercury is described,

which is sensitive to one part of mercury in 2 million parts of solution, and which by isothermal concentration at room temperature detects 1 part of mercuric ion per billion.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

THE VAPOR PRESSURES OF SOLID AND LIQUID CYANOGEN[1]

BY JOHN H. PERRY AND D. C. BARDWELL

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Previous Investigations

The vapor-pressure measurements of liquid cyanogen by Faraday[2] and by Chappuis and Riviére[3] cannot be considered very exact, as the purity of their material is uncertain, and precise thermometry had not been developed. A more extensive investigation has been made by J. W. Terwen[4] who measured vapor pressures of solid cyanogen to the triple point and liquid cyanogen to the critical temperature. Care was taken to obtain a very high purity of cyanogen and a sensitive platinum-resistance thermometer was used, but the low-temperature bath had a drift upward of 1° in five minutes at —70°. The drift was less at higher temperatures. Since the thermal conductivity of the solid is low there is some uncertainty as to the lag in temperature between the outer parts of the vapor-pressure bulb and the resistance thermometer at the center.

Preparation of Cyanogen

About 300 g. of C. P. mercuric cyanide was heated to 400° in a Pyrex flask which had previously been evacuated. The cyanogen evolved was passed through a tube containing phosphorus pentoxide and condensed in a bulb immersed in liquid air. With the bulb in liquid air, a small pressure on the manometer indicated some non-condensable gas, probably nitrogen, which was removed by a mercury-diffusion pump. The cyanogen was melted and frozen and the permanent gas pumped off until there was no residual pressure in liquid air. A preliminary set of measurements was made on the solid in the course of which it was observed that when the material was melted and then cooled to —89° there was a residual pressure of several centimeters above the vapor pressure of cyanogen. This residual gas was condensable in liquid air, which indicated that it was carbon dioxide. The most probable source of carbon dioxide is carbonate in the mercuric cyanide. Terwen[4] reported difficulty in removing nitrogen. It seems more plausible that carbon dioxide was one of the impurities in his gas. To remove this residual gas we fractionated the solid cyanogen at —88° to —92° until the pressure did not exceed 2 mm., that is, the vapor pressure of cyanogen, upon complete transfer of the

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[1] Published by permission of the Director of the Bureau of Mines, U. S. Department of the Interior.

[2] Faraday, *Phil. Mag.*, [1] **135**, 155 (1845).

[3] Chappuis and Riviére, *Compt. rend.*, **104**, 1504 (1887).

[4] Terwen, *Z. physik. Chem.*, **91**, 469 (1916).