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DETERMINATION OF MERCURY BY DIRECT HEATING OF MERCURY-ADSORBED ION-EXCHANGE RESIN IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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A new method has been devised for the determination of mercury in electrothermal atomic absorption spectrometry. The mercury-adsorbed ion-exchange resin was heated in a carbon furnace, and the absorption peak of mercury appeared in the "drying" period without interference from the peak of the resin. This method made it possible to determine 0.04ppm of mercury.

Preface

In earlier experiments the present authors devised a determination method which was carried out by heating and atomizing metal-adsorbed ion-exchange resin directly in atomic absorption spectrometry, and have already reported the results with respect to copper.1) This method made it possible to analyze an extremely dilute solution, but the precision was not satisfactry. The cause of the low precision is considered to be twofold: first, the appearance of an absorption peak in the "atomizing" period at the same position as the copper peak, even when H-type resin is heated in a graphite furnace; and second, the difficulty in weighing the small amount of resin put into the graphite furnace. The former can be avoided if the metal peak can be separated from the resin peak. Accordingly, in the present work the determination of mercury was attempted and a comparatively good result was obtained.

In the electrothermal method the volatilization of mercury is a matter of great importance, and various stabilizing methods have been examined.2)~6) The use of ion-exchange resin such as in the present method is considered to be effective not only for concentration of dilute solution, but also for stabilizing the volatilization of mercury.

Experimental

A two-channel atomic absorption spectrometer, designed by the present authors and assembled by Nippon Jarrel-Ash Co.Ltd., was used as a single-channel spectrometer. The resin used was H-type chelating ion-exchange resin transformed from Na-type Dowex A-1. The mercury salt was mercury (II) nitrate. All chemicals used were reagent grade.

Three hours after 0.1g of ion-exchange resin was put into a sample solution containing mercury (II) ion, the mercury (II) ion remaining in solution was measured. As the results showed that the remaining mercury increased when the pH value became small, the pH of the sample solution was adjusted to 5. Also, since co-existence of nitrate ion resulted in better adsorption of mercury ion onto the resin, the concentration of nitrate ion was adjusted to 10^{-1}M. Thirty minutes was enough time for the adsorption of mercury ion onto the resin in the present experiment. The resin, considered to be in a state of equilibrium, was dried in a desiccator after being washed with water. One mg of the dry resin was mounted in the graphite furnace by using the polyethylene adapter of a micro-pipette (Eppendorf type) with a few millimeters of the tip cut off for easier passage of the resin.

The resin adsorbed with mercury showed an absorption peak in the "drying" period, but the H-type resin did not. But even the H-type resin showed a peak when the "drying" current was high. This relationship is shown in Fig.1. According to this result, if the "drying" current is kept at 40~45A, the absorption peak of mercury can be measured without interference of the resin peak.

Results

The typical profile of absorption change was as is shown in Fig.2 when the resin was heated in a carbon furnace under the following conditions: "drying" current, 40~45A (10s); "ashing" current, 60A (45s); and "atomizing" current 230A (5s). The relation between the mercury peak height in the "drying" period and the mercury concentration in the sample solutions is shown in Table 1. The relation is linear; and although the curve passes a little above the origin, it can be used as a calibration curve.

This method made it possible to determine more dilute mercury solutions than by

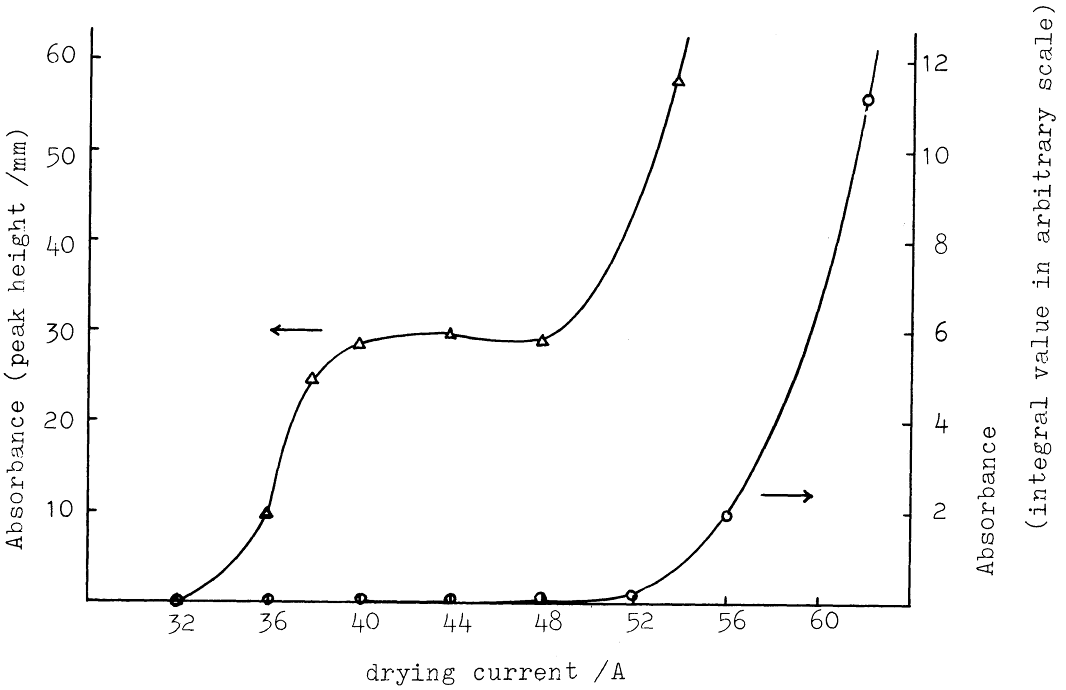

Fig.1 Absorbance change of mercury and resin at various "drying" currents.
Analytical line: 253.7nm; drying time: 10s; N_2 flow rate: 1l/min.
o: H-type resin, Δ: Hg-adsorbed resin

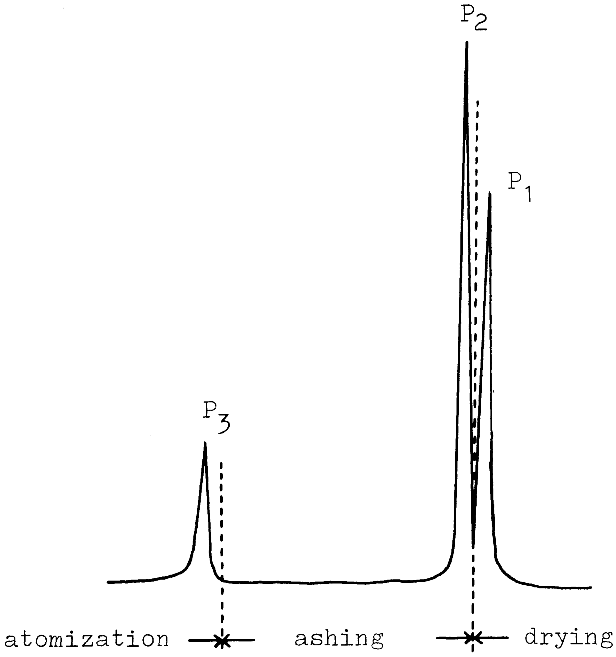

Fig.2 Typical profile of absorption of Hg-adsorbed resin in a graphite furnace at 253.7nm.
P_1: peak of Hg, $P_2 \cdot P_3$: peaks of resin

the usual electrothermal methods, and in the present experiment a solution of 0.04ppm concentration could be determined. It is believed that even more dilute solutions can be determined depending on the ratio of the amount of ion-exchange resin and the volume of sample solution.

Table 1 Experimental results

conc. of Hg (ppm)	sample vol. (ml)	average height of P_1 (mm)	number of measurements	standard deviation
0.037	100	10.55	4	2.8 (26.6%)
0.055	100	18.10	4	1.6 (8.6%)
0.073	100	25.54	5	3.5 (13.7%)
0.092	100	32.73	10	5.4 (16.3%)

Resin amount put into the sample solution : 0.1g

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