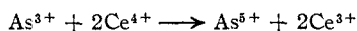


**CHRONOMETRIC CATALYTIC METHOD FOR THE DETERMINATION OF MICRO QUANTITIES OF IODINE**

Sir:

We have found that very small amounts of iodine as iodide can be detected and determined by making use of the catalytic effect of the element on the reaction between arsenious acid and ceric sulfate in sulfuric acid solution



In the absence of iodide this reaction proceeds with extreme slowness [cf. Browning and Cutler, *Z. anorg. allgem. Chem.*, **22**, 303 (1900); other literature references having a bearing on this matter will be considered in a detailed account of the method]. Traces of iodide increase the speed of the reaction enormously, the rate being directly proportional, or nearly so, to the iodide concentration, other factors being constant. Thus, if 1 ml. of potassium iodide solution containing 5 microgram of iodine is added to a mixture of 2 ml. of 0.1 *N* arsenious acid, 1 ml. of 0.1 *N* ceric ammonium sulfate, and 1 ml. of 6 *N* sulfuric acid, the reaction between ceric ions and arsenious acid is found to be complete in 0.9 to 1.0 min. (25°) as indicated by the disappearance of the yellow color of ceric cerium; with 2.5 microgram of iodine the time required for the reduction of the ceric cerium is 1.8 min. under the same conditions; with 1 microgram, 4.5 min., etc. In the absence of iodine the reaction requires 36 hours or more for completion. It is thus possible to determine the amount of iodide added by noting the time required for the yellow color due to ceric ions to disappear, since the time is inversely proportional to the amount of iodine present. The end-point of the reaction can be determined more precisely by using *o*-phenanthroline ferrous sulfate as indicator; the solution then assumes a pink color when the ceric cerium has been reduced, whereas the indicator is practically colorless in the presence of a slight excess of ceric cerium. Alkali chlorides and bromides, and other salts also, have a relatively slight effect, and by a special procedure it is possible to determine iodine in quantities ranging from 0.01 to 1 microgram in a dilution of 1:10<sup>7</sup> in the presence of 10<sup>5</sup> times as much chloride or bromide with an accuracy of about 20%.

The test is quite specific for iodine, since osmium and presumably ruthenium, are the only other elements showing similar behavior [cf. Gleu,

*Z. anal. Chem.*, **95**, 305 (1933)]. Micro quantities of osmium can be determined in the same way as iodine.

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**AN ISOTOPIC EXCHANGE BETWEEN H<sub>2</sub>O AND C<sub>2</sub>H<sub>2</sub>**

Sir:

Preliminary to the preparation of C<sub>2</sub>H<sub>2</sub> it was decided that a study of the possible isotopic exchange between acetylene and water was essential to the proper set up of a purification system. The weakly acidic character of acetylene has been demonstrated by several investigators,<sup>1</sup> as for example in the formation of metallic acetylides. Billitzer<sup>2</sup> claims to have evidence for an acetylenic anion. Accordingly we passed tank acetylene through a purification train as recommended by McIntosh<sup>3</sup> and then through water containing a high concentration of H<sub>2</sub>O. In the first experiment acetylene was bubbled for three hours at a rate of 3.5 liters per hour through about 3 cc. of water containing 18.5% of H<sub>2</sub>O. In order to minimize evaporation the bubble tube was immersed in an ice-bath and any vapor escaping was frozen out in a trap immersed in a salt-ice bath. The acetylene was swept out of the system by purified air in the first experiments and nitrogen was later substituted with no detectable change in results. The water in the trap and bubbler was combined and doubly distilled before the density determination. No detectable change in density was observed.

A similar experiment was carried out using 3 cc. of 18.5% solution of H<sub>2</sub>O to which was added sufficient anhydrous phosphorus pentoxide to make approximately a 1 *N* solution of phosphoric acid. After passing acetylene through this solution for five hours sufficient sodium oxide was added to more than neutralize the acid and excess alkalinity was removed by carbon dioxide. After the elimination of the gases the water was again doubly distilled and its density determined. Again there was no detectable change in composition.

To 3.5 cc. of 18.5% solution of H<sub>2</sub>O, enough sodium oxide was added to make the solution

(1) Keiser, *Am. Chem. J.*, **14**, 285-290 (1892); **15**, 535-539 (1893); Jones and Allen, *Chem. News*, **74**, 18-19 (1896); Bredig and Usoff, *Z. Elektrochem.*, **3**, 116-117 (1896).

(2) Billitzer, *Monatsh*, **23**, 489-501 (1902); **28**, 502-511 (1902).

(3) McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).