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TRIPYRIDYLTRIAZINE, A REAGENT FOR THE DETERMINATION OF IRON IN SEA WATER

By

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ABSTRACT

Iron, in the parts per billion range in which it occurs in sea water, can be determined spectro-photometrically with 2,4,6-tripyridyl-s-triazine (TPTZ). The intense violet compound formed by TPTZ and the ferrous ion is extractable into nitrobenzene if sodium perchlorate be added to the solution. The extraction affords a means of concentrating the iron from a large sample into a small volume of nitrobenzene for spectrophotometric measurement. The extraction also provides a means of removing the iron impurities from the solutions of the various reagents required, reducing agent and buffer, and thus of reducing the blank essentially to zero. If certain precautions are observed during analysis, particularly with respect to the cleaning of glassware, the absolute error is less than $0.1 \mu\text{g Fe/l}$.

INTRODUCTION

In an excellent paper published in this Journal in 1954, Lewis and Goldberg reviewed the problem of determining the minute amounts of iron in sea water and advanced the art by adapting to the determination the exceptionally sensitive reagent of Smith, *et al.* (1952): 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline). In the present paper a new reagent, 2,4,6-tripyridyl-s-triazine (Collins, *et al.*, 1959), equal in sensitivity to bathophenanthroline, is proposed for this determination. 2,4,6-tripyridyl-s-triazine (TPTZ) is easy to prepare (Case and Koft, 1959) and is much less expensive than bathophenanthroline. The violet ferrous derivative can be extracted into nitrobenzene; thus the reagent preserves the advantages of effecting a concentration of the iron and provides at the same time a means of removing any iron impurity from the various reagents.

The combining ratio of TPTZ and iron is two to one. The extraction of the violet ferrous derivate into nitrobenzene requires the presence of an excess of perchlorate; the extracted materials is

$\text{Fe}(\text{TPTZ})_2(\text{ClO}_4)_2$. The colorimetric measurements can be made either on the aqueous solution or on a nitrobenzene extract, the molar extinction coefficients being 22,600 at 593 $m\mu$ in aqueous solution and 24,100 at 595 $m\mu$ in nitrobenzene. The color conforms to Beer's Law in both solvents and is formed completely over the pH range 3.4 to 5.8; if nitrobenzene extraction is used, the permissible pH range is 2.7 to 7.0. TPTZ is slightly more sensitive than bathophenanthroline, for which the corresponding molar extinction coefficient is 22,400 in isoamyl alcohol. The solutions are completely stable for 12 hours and probably for an indefinite period. None of the common anions, including sulfate, chloride, nitrate, fluoride and perchlorate, cause interference in the determination of iron with TPTZ. The only metals which interfere are copper, cobalt and nickel, and these interfere only in concentrations a hundred-fold greater than those present in sea water; thus 2.5 ppm of copper, 2.4 ppm of cobalt, or 5.3 ppm of nickel are needed to produce an appreciable color with the reagent.

RECOMMENDED PROCEDURE

Reagents. 2,4,6-tripyridyl-s-triazine; 0.001 M. Dissolve 0.312 g of the tan, crystalline solid, with melting point 242–243.5° (G. Frederick Smith Chemical Company, Columbus, Ohio), in a few drops of hydrochloric acid and dilute to one liter with deionized water.

Hydroxylammonium chloride-sodium perchlorate solution. Dissolve 100 g of hydroxylammonium chloride and 100 g of sodium perchlorate in distilled water, mix, and dilute to one liter with distilled water. Transfer this solution to a large separatory funnel, add 10 ml of 0.001 M TPTZ and 25 ml of nitrobenzene, shake, and allow the layers to separate. Withdraw and discard the nitrobenzene layer. Repeat the extraction with nitrobenzene to make certain that all iron has been completely removed from the solution.

Sodium acetate-acetic acid buffer. Dissolve 82 g of sodium acetate and 58 ml of glacial acetic acid in distilled water, mix, and dilute to one liter with distilled water. Transfer the solution to a large separatory funnel, add 10 ml of 0.001 M TPTZ, 10 ml of hydroxylammonium chloride-sodium perchlorate solution and 25 ml of nitrobenzene, shake, and allow the layers to separate. Withdraw and discard the nitrobenzene layer. Repeat the extraction to insure complete removal of all iron.

Standard iron solution; $50 \mu\text{g Fe/l}$. Weigh accurately a quantity of about 0.1 g of electrolytic iron¹, dissolve in 20 ml of hydrochloric acid, transfer the solution to a one-liter volumetric flask, dilute to the mark with deionized water, and mix thoroughly. Pipet 25.0 ml of this solution into a one-liter volumetric flask, add 5 ml of hydrochloric acid, dilute exactly to one liter with distilled water, and mix thoroughly; this solution will contain approximately 2.5 mg or $2,500 \mu\text{g Fe/l}$. Pipet 20.0 ml of this solution into a one-liter volumetric flask, add 5 ml of hydrochloric acid, dilute to exactly one liter with deionized water, and mix thoroughly. From the initial weight of the iron, calculate the iron content of this solution, which will be about $50 \mu\text{g Fe/l}$.

Deionized Water. Pass distilled water through a column of Amberlite MB-3 ion exchange resin.

Procedure. Pipet 100.0 ml of the water to be analyzed (sea water, ground water, finished water or distilled water) into a 125-ml separatory funnel. Add 2.0 ml of iron-free hydroxylammonium chloride-sodium perchlorate solution, 5.0 ml of 0.001 M TPTZ, and 5.0 ml of iron-free buffer solution. If previous treatment of the sample, such as wet ashing, has introduced much acid, neutralize with ammonium hydroxide to pH 4 to 5. Add 10 ml of nitrobenzene, shake for one minute, allow the phases to separate, and then gently swirl the funnel to dislodge drops of nitrobenzene clinging to the upper walls. Drain the nitrobenzene layer into a 25-ml volumetric flask and repeat the extraction with another 10 ml portion of nitrobenzene. Dilute the combined extracts to 25.0 ml with ethanol. Determine the absorbancy of the solution at $595 \text{ m}\mu$, using 5-cm cells and a 4:1 mixture of nitrobenzene and ethanol in the solvent cell. Run a reagent blank through the entire operation and subtract its absorbancy from the absorbancy of the unknown solution.

Preparation of Calibration Curve. Pipet various volumes ranging from 0 to 50 ml of a standard iron solution containing $50.0 \mu\text{g Fe/l}$ into 125-ml separatory funnels, dilute each solution to 100 ml with deionized water, and carry on the analysis as described in the preceding paragraph.

¹ The electrolytic iron ignited in moist hydrogen (G. Frederick Smith Chemical Co.) comes in pieces 0.5–1 mm in size and the weight taken can be adjusted to within a few milligrams of 0.1 g; of course each lot must be weighed exactly.

RESULTS AND DISCUSSION

Inasmuch as the iron content of sea water has a tendency to change on standing by adsorption of iron on the walls of the container and because this work was carried out far inland, synthetic samples containing 10 ppm of fluoride, 3% of sodium chloride and varying amounts of iron were prepared and analyzed by the above procedure. The results shown in Table I were calculated using the calibration curve shown in Fig. 1.

TABLE I. DETERMINATION OF IRON IN SYNTHETIC SEA WATER, IN MICROGRAMS PER LITER

<i>Iron Added</i>	<i>Iron Found</i>	<i>Absolute Error</i>
0.70	0.70	0.00
3.49	3.40	0.09
6.89	7.35	0.37
10.47	10.4	0.1
13.96	14.2	0.2

Samples of treated water obtained from the Ames Municipal Water Works were also analyzed with the following results: 7.1, 7.3, 7.4 $\mu\text{g Fe/l}$.

Difficulty was encountered in the first few determinations, presumably because iron adsorbed on the glassware is only slowly leached away. It is recommended that the separatory funnels and

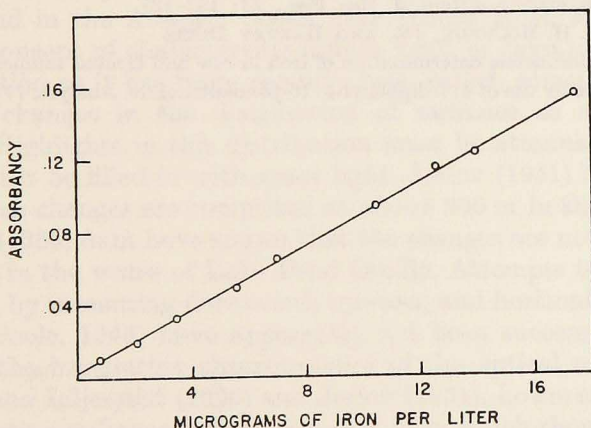


Figure 1. Calibration Curve for the Determination of Small Amounts of Iron in Water.

volumetric flasks used be rinsed with only deionized water between determinations and that they not be subjected to the usual cleaning methods. Pipets may be cleaned in a dichromate-sulfuric acid solution prepared from reagent grade chemicals.

As will be seen from the calibration curve (Fig. 1), the absorbancy values are relatively low, with little scatter; thus, small amounts of iron in water can be estimated with fair accuracy using TPTZ. This success arises from the sensitivity of the reagent, the concentration effected by the extraction, and the essentially zero blank obtained by cleaning up the reagents. In the recommended procedure, a concentration factor of four is obtained by the extraction; this can be increased by using a larger separatory funnel and a larger sample.

The main precautions which must be taken in this procedure are: 1) removal of iron from the reagents; and 2) conditioning the glassware by repeating the procedure several times before carrying out the actual determination.

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