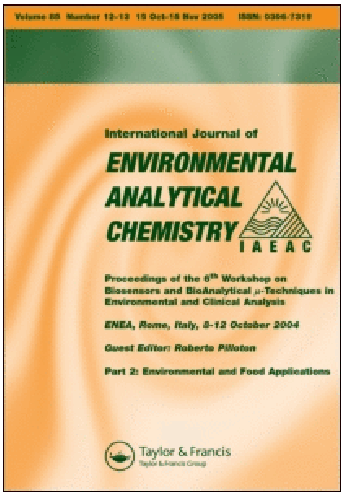

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Potentiometric Determination of Hg(II) Using 2-Thioorotic Acid (Amm. Salt): Application to a Chloroalkali Effluent

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POTENTIOMETRIC DETERMINATION OF Hg(II) USING 2-THIOOROTIC ACID (AMM. SALT): APPLICATION TO A CHLOROALKALI EFFLUENT

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2 - Thioorotic Acid (Amm. Salt) has been used as a selective reagent for the potentiometric estimation of Hg(II) ions at microgram levels, with an error of 0.4% at 5000μg/l, increasing up to 1.0 % at 100μg/l. The method has been found free from the interfering effects of Cl^-, Ca^{++}, Mg^{++}, and Fe^{++}, which are usually present in environmental samples, and applied successfully to the estimation of Hg(II) in chloroalkali effluents. Compared to the colorimetric dithizone method, the potentiometric method using the new reagent has been found to be more sensitive and simple in operation.

KEY WORDS: 2-Thioorotic acid, mercury (II), potentiometric titration, chloroalkali effluent.

INTRODUCTION

The methods reported for the potentiometric determination of Hg(II) include iodide[1-4], iodate[5], hexacyanocobaltic (III) acid[6], Cu(II)-EDTA complex[7], and tetraphenyl-arsonium chloride[8] as precipitants, and thiocyanate[9,10], thiosulphate[11], EDTA[12-14] and bis (2-hydroxyl) -dithiocarbamate ions[15] as complex forming reagents. Besides, reducing titrants such as Ti(III)[16], and Cr(II)[16,17] and V(IV)[18] have also been used. The mention of any application of these methods to environmental samples has, however, not been found. The instrumental techniques used are atomic absorption[19], spectrophotometry[19], emission spectroscopy[20] and neutron activation[21].

In the method described here, 2- thioorotic acid (amm. salt), has been used as a selective and highly sensitive precipitate forming reagent for the potentiometric estimation of Hg(II) in solutions and in chloroalkali plant effluents. The reagent gives a white precipitate, Hg $(C_5H_3N_2O_3S)_2$, with Hg(II) ions in neutral aqueous medium. The precipitate is stable and very sparingly soluble.

MATERIALS AND METHODS

Standardisation of procedure

2- Thioorotic acid was prepared by the method of Johnson and Schroeder [22], applying the Cannizaro's reaction to a chemically pure sample of 2-Thiouracyl-4-aldehyde. The ammonium salt of the synthesised compound was prepared by dissolving a weighed quantity of the compound in a minimum volume of concentrated ammonia. Insoluble particles were removed by filtration. The purity of the prepared salt was determined by mercurimetric estimation[22] using $Hg(NO_3)_2$ solution (BDH Analar grade), and was found to be 98.50%.

A potentiometric set up comprising a calomel half cell, platinum wire electrode and digital millivoltmeter(pla, Model DPM 10). The power supply was stabilized through a static voltage regulator (Suvik Model S.V.R. 6005). A stock solution of Hg(II) was prepared by treating 0.5015g of mercury (BDH Analar) with 10ml of distilled water and 5ml of concentrated nitric acid and heating to dryness. This was cooled and dissolved in distilled water and diluted to 250ml (1ml= 2.006mg Hg).

The stock solution was diluted to obtain concentrations in the range of 5000 to 5.0μg/l Aliquots (50ml each) of diluted solutions were taken in a 100ml beaker, and titrated potentiometrically with magnetic stirring, after adjusting the pH values of the substrate to 7.00 using dilute NaOH solution. Concentrations of Hg(II) above and below the range (5000μg/l - 5.0μg/l) were also used, but the peaks in these cases were not found to be sharp. The results of the potentiometric estimations have been shown in Table 1.

RESULTS AND DISCUSSION

Application of the method to a chloroalkali effluent

A sample (2.5 l) of the untreated form of effluent was collected from a chloroalkali plant located at Amlai (India). The physicochemical characteristics of the effluent were determined by standard methods[23] and were found to be as follows: pH 1.70, Na 170, K 11, Ca 100.2, Mg 36.5, and Cl 2473mg/l.

Aliquots (50ml) of the effluent were treated with diluted NaOH solution to pH 7.0. The solution, after filtration, was used for potentiometric estimation. The concentration of Hg(II) found is indicated in Table 1.

Comparison with the colorimetric dithizone method

The dithizone method is commonly used for the determination of Hg(II). However, the chloride ions which are invariably present in chloroalkali effluents (found at 2473mg/l here) pose serious interference problems. The filtered aliquots (50ml each) were repeatedly heated with concentrated H_2SO_4 till the chloride ions were eliminated as HCl gas. After adjusting

Table 1 Analysis data using potentiometry

Hg(II) solutions		*Titrant*		*Amount of Hg(II)*	*Percent*
Concentration (µg/l)	*Amount of Hg (II) present (µg/50ml)*	*Concentration* (µg/l)*	*Volume used (ml)*	*found (µg/50ml)*	*error*
Mercuric salt solutions					
5000	260.00	25000	16.90	249.10	0.4
2500	125.00	12500	16.95	124.40	0.4
1000	50.00	5000	16.95	49.73	0.5
500	25.00	2500	16.95	24.86	0.5
100	5.00	500	16.90	4.96	0.8
10	0.50	50	16.85	0.49	<2.0
5	0.25	25	16.30	0.24	<4.0
Chloroalkali plant effluent**					
		12500	17.10	125.42	

*After correction for impurities; 1ml (25000µg/l) = 14.66µg Hg; Stoichiometry $Hg(C_5H_3N_2O_3S)_2$

**Average value of 3 replicates

the pH between 1.0 - 2.0, the Hg(II) was extracted using a dithizone solution in carbon tetrachloride, and the absorbance measured at 490nm. A calibration graph was prepared by taking known quantities of $Hg(NO_3)_2$ dissolved in a synthetic diluent which contained all the constituents other than Hg(II) in concentrations present in the chloroalkali effluent. The mean value of six replicate estimations was found to be 2.50mg Hg/1.

Optimum conditions and interferences

Concentrations beyond 5000µg/l and below 5.0µg/l of mercury gave diffused peaks. The optimum concentration of the titrant for best results was found to be about five times that of the test solutions. A magnetic stirring during the titration is necessary. Neutral state of the reaction medium is preferred. However, variations within pH 5.5-7.5 have not been found to affect the accuracy of the determination. pH values higher than 7.5 have been found to have a solubilizing effect over the precipitated Hg(II) complex. At pH values lower than 5.5, the 2-thioorotate ions are transformed into 2-thioorotic acid which is insoluble. Chloride and sulphate ions are tolerated when present up to 2500 mg/l.

Hg(I) also forms sparingly soluble precipitate and interferes under the conditions of the experiment. Its interference can be removed by oxidising it to Hg(II), thus giving total mercury in the sample. Cu(II), Ni(II), Zn(II), Cd(II) and Fe(II) also react with the reagent forming slightly soluble precipitates[25-27], but during potentiometric titration the equivalence point of Hg(II) precedes the equivalence points of these ions. No interference up to 10-fold excess of these elements compared to the Hg(II)-level has been observed. Ag(I) interferes even at low concentrations, but it is rarely present in environmental samples.

CONCLUSIONS

The results obtained show that 2-thioorotic acid (amm. salt) can be effectively applied to the determination of mercury in chloroalkali plant effluents. None of the species present in this effluent interferes during the determination. The results obtained by this method showed good agreement (within 0.32%) with those obtained by the colorimetric dithizone method. The removal of the interference of chloride which is required in the dithizone method is not necessary in the new method. When applied to test solutions of Hg(II), the new method gave accurate results. The error was within 1% in the range of 5000-100µg/l of mercury, and increased to less than 4% at 5µg/l.

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