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Spectrophotometric Determination of Selenium (IV) Using Methdilazine Hydrochloride

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Methdilazine hydrochloride is proposed as a selective and sensitive reagent for the spectrophotometric determination of selenium (IV). The reagent forms a red radical cation by selenium (IV) in hydrochloric acid medium and exhibits an absorption maximum at 513 nm. Beer's law is valid over the concentration range 0.1-2.3 mg l⁻¹ of selenium (IV). Sandell's sensitivity of the reaction is found to be 3.57 ng cm⁻² and the molar extinction coefficient is 9.32 x 10⁴ l mol⁻¹ cm⁻¹ at 513 nm. The effects of acidity, reagent concentration, temperature and diverse ions upon the absorbance of the red species are critically assessed. The proposed method has been applied for the determination of selenium in alloys.

Introduction

Selenium is one of the trace elements which plays an active role in many biological systems¹ as it has toxicological and physiological effects^{2,3}. It has been reported on a large scale in specific geographical locations such as the People's Republic of China⁴. It is an essential nutrient at trace level but toxic in excess⁵. When selenium is present in animal feeds at a concentration less than 0.1 mg l⁻¹, deficiency symptoms develop, but when present at a higher concentration, exceeding 5 mg l⁻¹, chronic selenosis occurs. Selenium tends to weaken the toxic action of some heavy metals in animal and human organisms^{6,7}. A number of methods have been suggested for the spectrophotometric determination of selenium⁸⁻¹¹. Most of these methods suffer from limitations.

A literature survey showed that no attempt had been made to study the colour reaction of selenium (IV) with methdilazine hydrochloride, 10-(1'-Methyl-3' pyrrolidinomethyl) phenothiazine, (MDH) which forms a red radical cation on the oxidation by selenium (IV) at room temperature. A method has been developed for the rapid spectrophotometric determination of selenium in alloys.

Experimental

Equipment and reagents

A Hitachi UV-Visible spectrophotometer model 150-20 with 1.0 cm silica cells was used for absorbance measurements.

Selenium (IV) solution

A stock solution of selenium (IV) was prepared by dissolving AnalaR selenium dioxide (1.4 g) in 1 litre of water containing 10 mL concentrated HCl. It was standardised by the gravimetric method¹². The stock solution was further diluted as and when needed. A 0.2 % aqueous MDH solution was prepared and stored in a refrigerator. Solutions of diverse ions of suitable concentration were prepared using AnalaR reagents.

Procedure

Preparation of the calibration graph

An aliquot of the stock solution containing 2.5-57.5 μg of selenium (IV) was transferred into a 25 mL volumetric flask. Hydrochloric acid (20 mL of 10 M) and MDH (2 mL of 0.2%) were added. The solution was diluted up to the mark with distilled water and mixed well. The absorbance of the solution was measured after about 10 minutes at 513 nm against a reagent blank. The amount of selenium in the sample solution was then deduced from the calibration graph.

Determination of selenium in synthetic mixtures

In order to confirm the usefulness of the proposed method, it was applied to the determination of selenium (IV) in synthetic mixtures corresponding to selenium alloys, Se-Fe (42-51 % Fe), Se-Hg (71 %Hg) and Se-Pb (62 % Pb) which were prepared and the selenium content was determined by the procedure given above. The results are presented in Table 1.

Table 1. Determination of selenium (IV) in synthetic mixtures

Alloy	Se(IV)added mg l ⁻¹	Se(IV)found* mg l ⁻¹	Standard deviation
Hg-Se	0.70	0.71	0.003
	1.20	1.18	0.002
	2.10	2.08	0.005
Pb-Se	0.80	0.81	0.002
	1.50	1.52	0.003
	2.05	2.03	0.002
Fe-Se**	0.80	0.79	0.002
	1.40	1.43	0.003
	2.00	1.98	0.002

*Mean value of 5 determinations

**Passed through cation-exchange resin Amberlite IR-120 H

Results and Discussion

Preliminary investigations have shown that MDH reacts with Se (IV) at room temperature (27°C) in hydrochloric acid medium to give a red radical cation¹³. This was confirmed by passing an aliquot of the solution through cation exchange resin and an anion exchange resin. The cation exchange resin retained the red species confirming the cationic nature of the species.

Effect of acids

The effect of acids on the formation of a radical cation has been studied in HCl, H₂SO₄, H₃PO₄ and HNO₃ media. It is found that the maximum intensity of the radical cation is achieved in 8 M HCl in 10 minutes. The absorbance readings remained constant for more than 90 minutes. In the presence of other acids, maximum intensity of the colour cannot be reached, indicating the unstable nature of the coloured species in these media. All subsequent studies were carried out in 8 M HCl.

Effect of reagent concentration

Maximum intensity and constant absorbance readings are obtained in the presence of MDH (2 mL of 0.2 %). However, addition of excess of MDH has no appreciable effect.

Sequence of addition of reagents

From experiments in which Se, HCl and MDH were added in all possible sequences, it is found that there is no appreciable change in the colour of the species.

Validity of Beer's law, sensitivity and molar extinction coefficient

Beer's law is valid over the concentration range 0.1-2.3 mg l⁻¹ of Se(IV). The Sandell's sensitivity of the reaction as calculated from Beer's law data is 3.57 ng cm⁻² and the molar extinction coefficient is 9.32 x 10⁴ l mol⁻¹ cm⁻¹.

Precision and accuracy

The precision and accuracy of the method were studied by analysing solutions containing known amounts of Se (IV). The relative error is found to be less than 1.5%.

Effect of diverse ions

The extent of interference by diverse ions was determined by measuring the absorbance of solutions containing 2 mg l⁻¹ of Se (IV) and various amounts of diverse ions. The criterion for an interference was an absorbance value varying by more than ±2% from the expected value of selenium (IV) alone. The results presented in Table 2 show that a large excess of cations and anions, which are usually associated in the determination of Se (IV), do not interfere.

Table 2. Tolerance limits of diverse ions in the determination of 2 mg l⁻¹ of selenium (IV).

Ion or species added	Tolerance limit (mg l ⁻¹)	Ion or species added	Tolerance limit (mg l ⁻¹)
Hg(II)	50	Citrate	600
Ni(II)	800	Oxalate	500
Zn(II)	600	Nitrate	150
Mn(II)	700	Chloride	6000
Cr(III)	200	Acetate	4000
Pb(II)	3000	Sulphate	4000
Ca(II)	2000	EDTA	4800
Ba(II)	3600	Tartarate	6000

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