

Spectrophotometric determination of Ce(IV) using *o*-phenylenediamine in steels

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Abstract. A simple and sensitive spectrophotometric method for the determination of cerium(IV) was developed. With *o*-phenylenediamine cerium(IV) gives an orange-red colour with an absorption maximum at 470 nm. The system obeys Beer's law in the range 7 ppm to 500 ppm with a molar absorptivity of $2.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and Sandell sensitivity of 0.5 ppm. Interference by various ions was studied. This method was used for the determination of cerium in low-alloy steels and the results are in good agreement with the certified values.

Keywords. Cerium; *O*-phenylenediamine; Ce(IV) in steel; spectrophotometry.

1. Introduction

In a review of the literature on rare-earth additions to steel, Anderson and Spreadborough (1967) concluded that rare earths improve the quality and some mechanical properties of various types of steels, but that the exact effect depends on the nature of the steel. In general rare-earth additions to low-alloy steels improve the mechanical and plastic properties, besides acting as strong desulfurizing and deoxidizing agents (Kippenhan and Gschneidner 1970); whereas oxidation resistance and scaling resistance increase in the case of high-alloy steels. Addition of cerium alone increases the life of the steel. The amount of cerium added is critical and an excess is reported to have an adverse effect on high-temperature properties of steel (Trusou *et al* 1963).

The unique similarity in the chemical properties of the rare-earth group of elements has led to reliance on measurements of physical properties in order to obtain analytical data on mixtures of these elements. Various spectroscopic techniques have proven to be very useful (Fassel 1960) and among these optical emission spectroscopy has been the most widely used. However, the arc and spark emission spectra of the rare-earth elements are very complex and often consist of thousands of lines. As a result, line interferences are frequent and, even when high-dispersion instruments are used, interference-free lines are often difficult to find. Investigators were therefore led to explore the analytical capabilities of conventional flame which produces less complex spectra (Dean and Rains 1975).

Despite various attempts, it was not possible to determine cerium by atomic absorption spectroscopy (AAS) for a long period (Welz 1985). Kinnunen and Lindsjoe (1967) emphasized the difficulties in locating the proper rare-earth absorption line because of the complexity of the spectra emitted by hollow cathode lamps. They also reported that absorbance of several of the rare-earth elements was depressed significantly in the presence of fluoride and silicon. An indirect method (amplification

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reaction) has been reported for cerium by measuring molybdenum in molybdocero-phosphoric acid by AAS (Johnson *et al* 1973).

Traces of cerium are determined by titrimetric, kinetic, spectrophotometric (Sarma 1956; Papa *et al* 1959; Zhivopistsev and Parkacheva 1963; Pollock 1969; Arora *et al* 1980) and fluorimetric methods (Armstrong *et al* 1963; Kirkbright *et al* 1965, 1966; Cukor and Weberling 1968; Pal *et al* 1977; Poluektov *et al* 1970). Spectrophotometric determination in the visible range is best suited in routine analysis as the results are reproducible and the colour change can be conspicuously seen. A number of reagents are available for the spectrophotometric determination of cerium, such as brucine (Shemyakin and Volkova 1939), thenoyltrifluoroacetone (Hiroshi and Yukio 1965) and salicylhydroxime (Poddar *et al* 1965).

o-Phenylenediamine gives an orange colour with cerium(IV). The reaction is very sensitive and the colour is stable for quite a long time. Ce(III) does not give this test and hence does not interfere. A study of the above reaction was made for the spectrophotometric determination of Ce(IV) and the results are presented in this paper.

2. Experimental

2.1 Apparatus

Absorbance measurements were made with a Shimadzu 2100 S double beam UV-Vis spectrophotometer. pH measurements were made on a Unitech UI-11p pH meter.

2.2 Reagents

All reagents were of analytical reagent grade unless specified otherwise.

Cerium(IV) stock solution: 0.288 g of cerium(IV) sulphate was dissolved in 5 ml of sulphuric acid and made up to 100 ml to make a stock solution of 1000 ppm of Ce(IV). The solution was standardized gravimetrically (Vogel 1961).

o-Phenylenediamine (OPD) solution: 0.1% solution of the reagent was prepared by dissolving 100 mg of OPD (Koch-Light Laboratories Ltd, England) in 100 ml of distilled water and stored in an amber glass bottle.

2.3 Procedure

To 5 ml of 0.1% reagent (OPD) 2 ml of 1 M H₂SO₄ was added and the mixture was shaken well for 2 min. One ml of Ce(IV) solution containing 7 ppm to 500 ppm was added to the above solution. The mixture was made up to 10 ml with water and kept for 10 min to ensure complete reaction. The absorbance of the orange-red solution was measured against a similarly prepared reagent blank at 470 nm.

3. Results and discussion

The orange-red colour develops immediately on addition of reagent and the product is stable for 24 h.

Ce(IV)–OPD mixture showed maximum absorbance in the range 1 M to 3 M of H_2SO_4 after which the absorbance decreased. Five ml of 0.1% reagent was found to give maximum absorbance above which there was no significant increase in the absorbance.

The absorption spectrum of orange-red Ce(IV) and OPD products shows maximum absorbance at 470 nm, with a molar absorptivity of $2.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The system obeys Beer's law in the range 7 ppm to 500 ppm. Sandell sensitivity (Sandell 1959) of the colour was found to be 0.5 ppm of Ce(IV) at 470 nm.

3.1 Effect of diverse ions

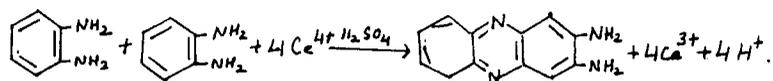
Effect of various ions on the determination of Ce(IV) by this method was examined. Fifty-fold excess of citrate, oxalate and tartrate showed no interference. Acetate, fluoride, phosphate, bromate, iodate, chloride, sulphate, nitrate, acetate and thiourea did not interfere. Hundred-fold excess of Pb, Cd, Mn, Al, Ti, Mo, W and U; fifty-fold excess of Co, Ni and Zn; and twenty-fold excess of Bi, Sn, Zr and Th did not interfere. Cu(II), Fe(III), Cr(III) and EDTA interfered seriously. Ce(III), La(III), Gd(III), Nd(III), Ho(III), Yb(III) and Dy(III) did not interfere.

3.2 Precision

The precision of the determination of Ce(IV) by the present method was evaluated by analysing replicate samples containing different concentrations of Ce(IV) (each determination was carried out six times). The relative standard deviation in the range 2.51–1.02 for 250–100 ppm of Ce(IV) indicates that the method is very precise.

3.3 Composition and mechanism

Job's (1928) method of continuous variation shows no complex formation which is also confirmed by IR spectra. Hence the most possible mechanism can be the oxidation of OPD by Ce(IV). The oxidation product formed can be a diaminephenazene. The possible reaction is:



4. Analytical application

Dissolution of steels: Weigh (0.25 g) of the steel sample and transfer it to 250 ml beaker. Add 30 ml of HCl (sp. gr. 1.13) and heat till sample is dissolved. Add HNO_3 dropwise continuously, avoiding any excess, until iron is just oxidized, indicated by slight effervescence. Boil the solution till the fumes are clear. Cool the solution. Iron and manganese were separated (Luke 1966; Burkin 1980) prior to the determination of Ce(IV). The solution (free from iron and manganese) was boiled with H_2SO_4 and $(NH_4)_2S_2O_8$ so as to ensure complete oxidation of Ce(III) to Ce(IV). Ce(IV) in the

Table 1. Analysis of low-alloy steels for cerium.

Steel sample/composition (%)	Certified value (%)	Cerium found* (%)	
		Present method	AAS#
(A) ST02-1 C = 0.101; Si = 0.64; Mn = 0.22; S = 0.0048; Cu = 0.070; Ni = 0.082; Cr = 4.10; Mo = 0.53; V = 0.41; Ti = 0.029; Co = 0.018; Sn = 0.066; Nb = 0.11; Sb = 0.010; Ta = 0.063	0.0580	0.0562	0.0578
(B) ST03-1 C = 0.159; Si = 0.46; Mn = 0.75; S = 0.010; Cu = 0.67; Ni = 0.17; Cr = 3.23; Mo = 0.39; V = 0.019; Ti = 0.062; Co = 0.15; Sn = 0.046; Nb = 0.069; Sb = 0.011; Ta = 0.012	0.0120	0.0117	0.0118
(C) A-1 C = 1.01; Al = 0.01; Ni = 4.00; Ti = 0.27; Nb = 0.200; Pb = 0.036; W = 0.16	0.0240	0.0240	0.0243

* Average of six determinations

Johnson *et al* 1973

solution was determined by the proposed method. The results show fairly good agreement between the proposed method and the certified value (table 1).

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