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ENTHALPIMETRIC ASSAY OF CERIUM-IRON ALLOYS

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Direct injection enthalpimetric determination of cerium/IV/ and iron/III/ were performed sequentially in the same solution of ferro-cerium alloys using potassium iodide and sodium thiosulphate solutions.

Cerium metal alloys are used widely in the steel industry for the production of ductile iron cast steel, some special alloy steels as pyrophaic alloys, as well as for the removal of traces of nitrogen and oxygen from sealed vacuum systems.

There have been methods available for the determination of milligram amounts of cerium and iron in admixture for some years. These have included routine use of automated XRF as well as titrimetric methods. The latter are preferred for semi-routine use or when the number of samples does not warrant the large capital expenditure and running costs of the XRF procedure. General titrimetric methods have been reviewed by Salutsky [1]. The titrimetric methods for the determination of cerium in the presence of iron are often based on the oxidative dissolution of the alloy and then the determination of cerium as Ce(IV) in the presence of iron(III) and often involve the reduction of the Ce(IV) with an excess of iron(II) with subsequent determination of the excess of the iron(II) with Mn(VII).

Methods for the determination of both iron and cerium generally involve the determination of cerium or iron on one sample, and then the total iron and cerium on a second sample; the individual constituents are then determined by difference [2, 3]. The overall time for the assay is necessarily lengthy.

We have investigated a method for the determination of cerium and iron on the same sample by a simple, rapid, easily automated method.

The oxidation of iodide to iodine by Ce(IV) ions has been previously reported [4].

The oxidation of iodide by Fe(III) ions is a slow reaction whose kinetics have been extensively studied [5]. For general titrimetric work it is necessary to catalyse the reaction in order that the iodine is liberated in a convenient time, and the determination of Fe(III) via I is a well established method [6]. In general analysis, iodometric determinations are most often made indirectly because of the difficulties of end-point detection in classical titrimetric techniques.

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It has been established that many redox reactions have relatively large heats of reaction [7]. To a large extent this is the direct consequence of large entropy changes involving ionic and molecular solvation. Such effects are advantageously used in thermometric and enthalpimetric analysis. However, the determination of molecular iodine, liberated as a result of a redox reaction, by titration with thiosulphate is not generally considered to be a useful thermometric technique. This is becasue of the relatively large endothermic heat of dilution of the concentrated sodium thiosulphate used as the titrant. This gives a low overall heat of the reaction (ca. 5–10 kJ mol^{-1}). It is, however, possible to use a „doped" solution of thiosulphate having a zero heat of mixing or dilution, viz. a thermally neutral solution, in order to obtain a satisfactory indication of the large heat of the redox reaction between molecular iodine and thiosulphate.

Preliminary experiments indicated that release of iodine in an excess of potassium iodide was sufficiently exothermic to be used with suitable precision in the types of solution generally found in the analysis of cerium-containing alloys. The amount of heat generated by the slow reaction of potassium iodide with iron(III) ions is negligible compared with that generated in the rapid reaction between cerium(IV) and iodide ions during the time of the latter reaction. Therefore, one can make use of this to determine cerium(IV) by direct injection of potassium iodide into the solution of the alloy. The heat liberated may then be assumed to correspond solely to the amount of cerium(IV) present. By use of a suitable catalyst, the iron(III) may then cause release of a stoichiometric amount of iodine from the excess of potassium iodide present. The total amount of iodine liberated thus corresponds to the total of the cerium(IV) and the iron(III) present. This liberated iodine may then be determined using a thermally neutral solution of sodium thiosulphate.

Interferences

There are three classes of substances which could possible interfere with the procedure:

(a) Substances which concurrently with the Ce(IV) ions oxidise the iodide ions.

(b) Substances which form complexes with the excess of the iodide present, with a consequent heat of reaction.

(c) Substances which could interfere with the catalysed reaction between the iodide ions and the iron(III) ions.

These, (c), may be either those which enhance the reaction by acting as a superior catalyst or those which react with the iron(III) ions or the copper(I) ions which are used as the main catalyst. The effects of potential interferents were examined.

A method suitable for the determination of milligram amounts of Ce/Fe alloy was then devised. The usual analytical parameters regarding accuracy, reproducibility were systematically investigated.

Experimental

The details of the apparatus used for the direct injection enthalpimetry, including the design of the submersible pipettes and the Wheatstone Bridge/Thermistor circuit, have been previously reported [8]. In some experiments designed for the routine batch analysis of alloys the potentiometric recorder was replaced with a digital voltmeter fitted with a rheostat as an external shunt, of resistance such that the whole bridge system could be so adjusted that a standard sample gave 100 units for either iron or cerium, after suitable adjustment of the rheostat.

Solutions

For calibration purposes an acidified aqueous solution of ammonium sulphato cerate(IV) was standardised against As(III); the iron(III) solution was standardised against EDTA by thermometric methods.

Potassium iodide

A 25% w/v aqueous solution of reagent grade potassium iodide was used throughout.

Copper(I) catalyst

A saturated solution of copper(II) sulphate (5 cm^3) was treated with an excess of the 25% w/v potassium iodide solution. The precipitate was washed with water, by decantation, until the washings did not give a coloration with starch solution. The solid residue was suspended in water (50 cm^3) and aliquots of this, freshly stirred, were used in all experiments.

Thermoneutral sodium thiosulphate solution

In order to obtain a concentrated sodium thiosulphate solution, which had a zero heat of mixing with water, it was necessary to use a mixed water: glycerol solvent.

The composition of the solution used was 35% w/v $Na_2S_2O_3.10H_2O$ dissolved in a 1:1 water: glycerol solution. (Density 1.25–1.26 at 20^o.) (This composition was found by trial and error.)

Procedure

Transfer an aliquot of the solution used for calibration (20 cm^3 of an appropriate composition of cerium and iron with molar ratios of Ce:Fe between 30:1 and 1:30) to the thermostatted cell of the titrator. Using a submersible pipette, place a fixed volume of 25% w/v potassium iodide solution (nominally 2 cm^3) below the surface of the Ce/Fe solution.

Submerge a second pipette, containing 2.0 cm^3 of the thermoneutral sodium thiosulphate solution, below the surface of the sample solution.

Determination of the cerium(IV)

Stir the mixture, and when thermal equilibrium has been established (as indicated by a steady base line on the recorder chart) inject the potassium iodide solution into the metal solution and note the heat pulse registered.

The amount of Ce(IV) present is then calculated from the appropriate calibration graph.

Determination of the iron(III)

To the above mixture add 0.5 cm^3 of copper(I) iodide suspension. When the trace shows that thermal equilibrium has been established, inject the sodium thiosulphate solution and measure the heat pulse recorded.

Table 1 Amount of cerium(IV) found in the presence of constant amount of iron(III)

Amount of Ce(IV), mg		% Difference	Amount of Ce(IV), mg		% Difference
taken	found		taken	found	
31.4	31.8	1.28	85.6	86.0	0.47
31.4	32.0	1.91	85.6	86.0	0.47
42.8	42.8	0.00	99.8	100.4	0.60
42.8	42.7	0.23	99.8	100.4	0.60
49.9	49.7	0.40	114.1	113.6	0.44
49.9	50.4	1.00	114.1	114.6	0.44
57.0	58.1	1.93	128.3	128.4	0.08
57.0	57.4	0.70	128.3	127.4	0.70
64.2	64.4	0.31	142.6	143.2	0.42
64.2	64.4	0.31	142.6	142.2	0.28

Amount of iron(III) added = 0.0160 grammes and each composition was determined in duplicate, viz. a ratio of Fe:Ce of 1:7.5 x 10^{-2} to 1 to 3.5 x 10^{0}.

The total amount of cerium and iron is determined by reference to the appropriate calibration graphs.

The amount of iron present is then calculated by difference.

Determination of mixtures

Synthetic mixtures of the two substances ammonium cerato(IV) nitrate and iron(III) nitrate were prepared.

One series contained a constant amount of iron(III) and various amounts of cerium(IV) (Table 1).

One other series contained a constant amount of cerium(IV) and various amounts of iron(III) (Table 2).

A third series contained various amounts of each ion (Table 3).

Each of these series was assayed by the proposed method. A typical enthalpogram is given in Fig. 1.

Table 2 Amount of cerium(IV) found in the presence of various amounts of iron(III).

Fe(III) added, mg	Ce(IV) found, mg	% Difference	Fe(III) added, mg	Ce(IV) found, mg	% Difference
16.0	24.3	0.82	166.0	24.3	0.82
16.0	24.3	0.82	166.0	24.3	0.82
62.0	24.4	0.41	224.0	25.1	2.45
62.0	24.3	0.82	224.0	25.1	2.45
83.0	24.9	1.63	280.0	24.7	0.82
83.0	24.7	0.82	280.0	25.1	2.45
104.0	24.7	0.82	336.0	24.7	0.82
104.0	24.7	0.82	336.0	24.3	0.82
140.0	25.1	2.45	420.0	24.7	0.82
140.0	24.9	1.63	420.0	25.1	2.45

Amount of cerium(IV) taken 0.0245g and each composition was determined in duplicate, viz. $1.75 \times 10^{-4} M$ Ce in a range of $2.8 \times 10^{-4} M$ to $7.5 \times 10^{-3} M$ iron.

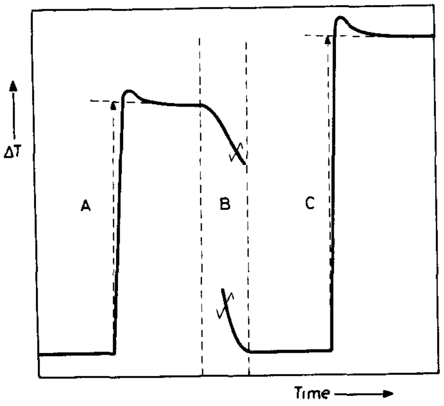

Figure 1 Enthalpogram showing heat pulse, plateau and endothermic heat effect when iodine liberated by Cu_2I_2 catalymetric reaction. A: KI injection (determination of Ce/IV/); B: Cu_2I_2 addition – liberation of I_2 by Fe/III/; C: $Na_2S_2O_3$ injection – determination of total oxidants present

Table 3 Analysis of mixtures of cerium(IV) and iron(III) over the range (1–2) x $10^{-5}M$ Ce with (3–5 x $10^{-4}M$ Fe.

Amount of Ce(IV), mg		% Difference	Amount of iron(III), mg		% Difference
taken	found		taken	found	
14.3	14.5	1.40	16.0	16.2	1.23
19.6	19.8	1.02	42.5	42.0	1.17
21.4	21.6	0.93	16.0	16.2	1.23
23.5	23.3	0.85	42.5	42.1	0.94
28.5	28.5	0.00	16.0	15.7	1.87

Triplicate determination for each composition and an average result is reported.

A fourth series containing various amounts of each ion was assayed both by the proposed method and by a classical titrimetric method [1] which required two titrations; first the iron was masked by the addition of sodium polyphosphate and the cerium(IV) was used to liberate iodine from acidified potassium iodide. The second titration, using a separate sample, involved the liberation of iodine from acidified potassium iodide by both the cerium(IV) and the iron(III). In both titrations the iodine liberated was determined using sodium thiosulphate as titrant and starch solution as indicator.

These results are given in Table 4.

Interferences

1. A search of the available literature did not reveal any systems, other than Cu(I)/Cu(II), as catalysts for the iron(III)/iodide ion reaction. Ligands such as fluoride, cyanide, thiocyanate and anions from derivatives of iminodiacetic acid are unlikely to be present before or after the dissolution of the cerium/iron alloys and hence will not react with the copper(I) or the iron(III) present.

Table 4 Results obtained from duplicate determination of cerium(IV) and iron(III) in admixtures by DIE and volumetric titration (iodometric method).

Mixture of	Amount in mg		
	taken	found	
		DIE	volumetric
Ce	14.0	14.2	13.9
Fe	78.4	77.9	77.6
Ce	28.0	28.5	27.6
Fe	67.2	66.5	66.8
Ce	42.0	42.0	41.5
Fe	56.0	55.8	55.4
Ce	56.0	56.1	55.0
Fe	39.2	38.6	38.7
Ce	70.0	70.3	69.6
Fe	22.4	22.4	22.3

2. A survey of the standard electrode potentials of any possible redox systems indicated that for practical purposes, unless Au(III) were present, none of the ions likely to be present would, concurrently with Ce(IV), oxidise the iodide ion to iodine.
3. Substances which could possibly form complexes with the excess of iodide ions, such as Sn, Hg, Cd, are unlikely to be present in the alloy and hence may be ignored.
4. Other materials likely to be present after dissolution of the sample in hydrochloric acid are sulphate, nitrate and phosphate, and trace amounts of other alloying elements.

From a consideration of the composition of some commercially available alloys a study of the effects of possible ions was made (Table 5).

Proposed method for the analysis of ferro-cerium alloys

Dissolve a known weight of the alloy (containing approximately 20 mg Ce/40 mg Fe) in sulphuric acid (10 ml of 25% v/v aqueous sulphuric acid).

Add ammonium persulphate solution (5 ml of 10% w/v aqueous solution). Heat the mixture to boiling and boil for 5–7 minutes until all the persulphate is decomposed (starch-iodide test). Cool the solution, transfer to a graduated flask and adjust the volume to 25 ml with water. Pipette 20 cm^3 to the thermostatted cell of the titrator. Using a submersible pipette, place a fixed volume of 25% w/v potassium iodide solution (nominally 2 cm^3) below the surface of the Ce/Fe solution.

Submerge a second pipette, containing 2.0 cm^3 of the thermoneutral sodium thiosulphate solution, below the surface of the sample solution.

Determination of the cerium(IV)

Stir the mixture, and when thermal equilibrium has been established (as indicated by a steady base line on the recorder chart) inject the potassium iodide solution into the metal solution and note the heat pulse registered.

The amount of Ce(IV) present is then calculated from the appropriate calibration graph.

Determination of the iron(III)

To the above mixture add 0.5 cm^3 of copper(I) iodide suspension. When the trace shows that thermal equilibrium has been established, inject the sodium thiosulphate solution and measure the heat pulse recorded.

The total amount of cerium and iron is determined by reference to the appropriate calibration graphs.

The amount of iron present is then calculated by difference.

Table 5 Effects of various ionic species on cerium(IV) recovery (a)

Ionic species added	mg	% Error	Ionic species added	mg	% Error
Ag(I)	0.4	+1.4	Cr(VI)	0.1	+1.3
Al(III)	102	−1.2	Mn(VII)	0.1	+4.7
Bi(III)	2.5	+2.0	Th(IV)	124	+0.7
			Ti(IV)	175	−2.0
Co(II)	159	−0.9	Zn(II)	180	+1.3
Cu(II)	40.0	−1.3	Zr(IV)	66	−2.1
Fe(III)	114	+0.44	PO_4^{3-}	9.5	−6.7
La(III)	133	+0.5	$S_2O_8^{2-}$	19.2	+10.6^x
Mg(II)	124	+0.5	SO_4^{2-}	2000	±1
Ni(II)	129	−1.3	NO_3^-	62	+0.2

^{x}Although persulphate gives a massive interference, the method of preparation of the sample involves removal of the persulphate ion by boiling the solution. It was found that 5–7 minutes' boiling removed the persulphate (tested for using starch-iodide paper).

Determination of the precision of the method

A sample of an alloy was prepared by melting together 4.40 g of cerium metal, 8.50 g of pure iron wire and 7.10 g of magnesium powder. The melt was agitated to produce homogeneity. The cold alloy was then drilled under an atmosphere of dry nitrogen at a temperature approximately that of acetone/solid CO_2. Random samples of approximately 100 mg weight were dissolved in sulphuric acid, 10 ml of 25% v/v sulphuric acid and then oxidised with persulphate (5 ml 25% w/v ammonium persulphate in water) and the solution was boiled for 5–7 minutes until the excess of the persulphate was decomposed.

The prescribed method was then followed.

Results

11 samples were taken, the weights ranging from 102 mg to 95 mg. The results, normalised for 100 mg of sample, viz. 22.0 mg of cerium, 42.50 mg of iron, varied

between 21.60 and 22.58 for Mg with a standard deviation of 0.246 mg, and for iron between 41.70 and 43.20 mg with a standard deviation of 0.51 mg.

Discussion of results

For methods which are to be used in routine analysis there are several criteria which must be met before any method may be considered to be acceptable. It is necessary that the overall time for the determination be as small as possible in order to allow the maximum number of samples to be assayed during the production period. Thus the speed of the determination, the general ease of automation of the method, the average reproducibility on the same sample, the effects of small variations in the composition of the sample presented for assay by the proposed method and the overall costs of the method are all of significance.

The main purpose of the proposed method is to enable the assay of ferro-cerium alloys and magnesium-cerium alloys generally with a cerium content of between 3%–50% by weight.

The apparatus used can be readily connected to a controlled and programmed apparatus similar to that described by Guillot [9] and it is thus possible to construct an automatic direct reading system for the continual batch determination of cerium and iron in solutions prepared for suitable alloys.

It may be seen from Table 5 that variations of the type and order commonly found in different batches of cerium-iron alloys do not have any significant effect on the values obtained for the cerium(IV) and iron(III) contents of the alloys. The method is also applicable in the presence of a fairly wide range of foreign ions not commonly encountered in the alloys considered.

The cerium(IV) and the iron(III) are determined sequentially in the same solution. The time for the various steps is as follows: presentation of an aliquot of the solution to the reaction vessel (ca. 1 min); a waiting period in order to allow thermal equilibration (3 min), titration of the cerium(IV) by DIE (2 sec), addition of the copper(I) catalyst, and a waiting period in order to allow thermal equilibration and complete liberation of the iodine (15 min); injection of the thiosulphate solution (2–3 sec). Washing and draining require approximately 2 min. Thus the overall time is about 20 min.

If the classical method is used, the time-determining step is the liberation of iodine by the cerium(IV) and iron(III) and then added to this the titration of the liberated iodine. (It is assumed that the period of liberation of iodine is used for the separate determination of the Ce(IV) content of the solutions in which the iron(III) has been masked by polyphosphate.)

The overall time is not much different but the overall work load is much less for the automated method and hence a saving is generally made in total laboratory costs.

One other advantage is that there is only one sample solution required for both the cerium and the iron determinations and there is no need for precise standardisation of any titrant solutions [1] in the enthalpimetric methods.

The overall accuracy is not as high as can be achieved by the classical method but is still within that acceptable for routine assays.

We thus suggest that the overall advantages lie with the proposed method.

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Zusammenfassung — Eine direkt injektionsenthalpimetrische Bestimmung von Cerium(IV) und Eisen(III) Ionen nacheinander in der selben Lösung von Eisen-Cerium Legierungen mit Kaliumjodid und Natriumthiosulphat als Masslösung wurde erfolgreich ausgeführt.

Резюме — С помощью растворов иодида калия и тиосульфата натрия проведено прямое энтальпиметрическое последовательное определение ионов четырехвалентного церия и трехвалентного железа из одного и того же раствора ферро-цериевых сплавов.