

## ENTHALPIMETRIC ASSAY OF CERIUM-IRON ALLOYS

*L.S. Bark and V. Opasniputh\**

RAMAGE LABORATORIES, UNIVERSITY OF SALFORD SALFORD, M5 4WT, UK; \* CHIANG-MAI UNIVERSITY, THAILAND

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 pyrophoric 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<sub>2</sub> 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.

\* All correspondence to L. S. Bark

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 because 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.  $5-10 \text{ kJ mol}^{-1}$ ). 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 possibly 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.