

Valence Analyses of Elements

UV absorbing dopes in quartz

In modern Xenon light bulbs for automotive applications, elements like Cerium (Ce) and Europium (Eu) are used in the quartz sleeve to intercept harmful UV radiation. For optimal performance the Ce has to be in the trivalent state and Eu in the divalent state. By applying both Ce and Eu, UV radiation between 180 and 400 nm is effectively absorbed. For optimal performance Ce(III) is added as Ce-Si-oxide and Eu(II) is added as Eu-Al-oxide. To ensure these lower valences, the oxides are prepared under reducing atmosphere. Chemical analysis is used to determine the efficiency of this reduction process.

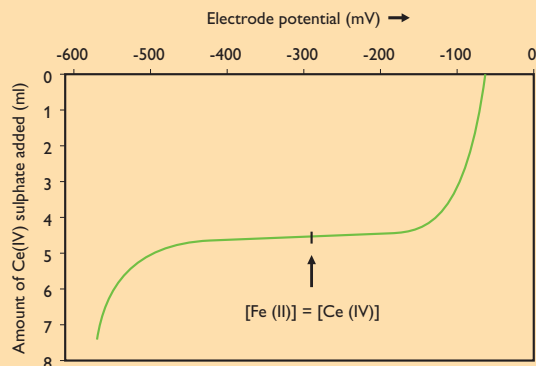


Fig. 1: Potentiometric titration of Fe(II) with Ce(IV) solution, showing the variation of electrode potential during the titration.

Redox titrations

The most efficient technique to determine valence states of elements is redox titration. After dissolution of a sample in acid, the elements of interest react with a redox couple that is added to the solution. In most cases the Fe(II)/Fe(III) redox couple is suitable for this purpose. In the case of the Eu(II) dope, the Eu(II) is oxidized to Eu(III), because the redox potential of the Fe(II)/Fe(III) couple is higher than that of the Eu(II)/Eu(III) couple:

$$\text{Eu}^{2+} + \text{Fe}^{3+} \rightarrow \text{Eu}^{3+} + \text{Fe}^{2+}$$

The amount of Fe(II) formed is equivalent to the Eu(II) concentration and can be determined by a potentiometric titration with a standard Ce(IV)-sulphate solution. Figure 1 shows a titration curve of this titration and the frontpage (left) depicts the equipment used.

In the case of the Ce(III) dope, direct determination of Ce(III) is not possible, but the amount of unwanted Ce(IV) can be determined in a similar way.



Fig. 2: Carius tubes filled with HCl + Fe(II) before (colourless) and after (yellow) reaction with Ce(IV). The orange colour represents a higher concentration of Ce(IV)-sulphate.

Analytical procedure

Dissolution of the samples is required and has to take place under a fully inert atmosphere to prevent oxidation by oxygen from the air. Samples are dissolved in so-called carius tubes; glass tubes to which hydrochloric acid with a known amount of Fe(II)/Fe(III) is added. The tubes are closed by melting under argon atmosphere. Subsequently, the tubes can be heated up to 200°C to dissolve or decompose the samples. Figure 2 shows such carius tubes before and after reaction. After dissolution the tubes are cooled, opened and the solution is transferred to a titration vessel (frontpage) and titrated under argon atmosphere with a Ce(IV)-sulphate standard solution.

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Accuracy

In the case of Eu(II) analysis, where the main component is determined, the accuracy of the analysis is particularly important. This can be as good as $\pm 1\%$ relative, depending on the homogeneity of the sample. In the case of Ce(IV) analysis, the unwanted impurity component is determined, so apart from accuracy, the lower limit of determination is also important. For the Ce(III)-Si-oxide doping material this can be as low as 0.01 weight % Ce(IV).

Conclusions

Redox titration is a powerful technique for quantitative analysis of valence states of elements. Depending on the elements and the sample material, an optimal choice of dissolution procedure and redox couple can be made. As a result, this technique can be applied to many areas. Apart from the UV absorbing dopes for quartz, shown in this Application Note, the method has been applied to battery materials, ferrites, ceramic superconductors and many oxide materials for which the valence state is important.



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