

X-ray Spectrometric Determination of Ceria-Yttria Mixtures after Borate Fusion

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X-ray fluorescence analysis after automated borate fusion of the analyte with lithium tetraborate was investigated as a potentially fast and accurate method to characterize ceria-yttria mixtures for fuel cell applications. Because ceria-yttria powder mixtures can be prepared in several ways that lead to products with different particle sizes, fusion of the sample was desirable. In this way, X-ray analysis can be used to characterize both the homogeneity and the chemical composition of the oxide mixture which are important to control in fuel cell applications. Correction for interelement X-ray absorption effects in the fused specimens was performed with NRLXRF using as few as two standard samples for calibration. For best results, the sample-to-flux ratio should be held constant and a correction for infinite thickness should be applied if the $K\alpha$ line of yttrium is chosen for measurement. Analysis of Y_2O_3 (12–85 %) and CeO_2 (15–88 %) in these mixtures was performed with a relative error of less than $\pm 1\%$.

Oxide solid solutions having a defective fluorite structure such as CeO_2 , ZrO_2 , and ThO_2 , doped with trivalent oxides such as Y_2O_3 have high oxygen ion mobilities relative to the pure constituent oxides. This property makes these solid solutions potentially useful as solid electrolytes in high-temperature fuel cells. The high oxygen mobility results from the large concentration of oxygen vacancies introduced into the oxygen sublattice when from 5 to 15 mol % of the dopant is added to the host oxide system.

The obtained Y-doped ceria suitable for this application requires the development of methods for preparing ceramic specimens which possess high density, uniform microstructure, homogeneous composition, and high purity. Several chemical procedures were investigated for preparing well-mixed and reactive ceria-yttria powders of known composition (1). These include coprecipitation from homogeneous solution and mechanical mixing of known proportions of the individual calcined powders. To assess the chemical composition of the mixed powder as a precursor for preparing a Y-doped ceria ceramic by hot-pressing, X-ray fluorescence spectrometry was investigated as a convenient method for analysis. Because the particle size of the resultant powder mixture depends on the method of preparation, it was decided to employ automated fusion of the powder mixture with lithium tetraborate to eliminate any particle size effect which is inherent in a direct analysis of powdered materials by X-ray spectrometry. Although various publications (2–4) have appeared describing the XRF analysis of rare earths in powder form, only three

Table I. Analysis of CeO_2 - Y_2O_3 Mixtures with and without Correction for Infinite Thickness for Y_2O_3 ^a

sample	% CeO_2 present	% CeO_2 found	% Y_2O_3 present	% Y_2O_3 found ^b	% Y_2O_3 found ^c
CY3	77.26	77.22	22.74	22.93	22.85
CY4	76.87	76.82	23.13	23.17	23.11
CY6	88.08	88.21	11.92	11.97	11.97
CY7	60.08	60.23	39.92	40.49	40.25
CY8	59.97	59.93	40.03	40.64	40.40
CY9	14.75	14.83	85.25	85.44	85.41
ARE ^d				0.81	0.47

^aNRLXRF and two standards for calibration CY2 = 14.24% CeO_2 , 85.76% Y_2O_3 and CY5 = 88.27% CeO_2 , 11.73% Y_2O_3 . W tube, 60 kV. Weight of oxide mixture = 0.35 g; $Li_2B_4O_7$ = 6.2 g. ^bNo infinite thickness correction. ^cWith infinite thickness correction. ^dARE, average relative error.

papers were found which reported on the analysis of such materials after borate fusion (5–7).

This present work was performed in order to seek a rapid XRF method for the analysis of rare earths and lanthanides as major components with an accuracy limited principally by the automated fusion sample preparation technique. The interelement X-ray absorption effects in the fused specimens were corrected using the fundamental parameter program NRLXRF (8), with only two standards for calibration. It will be shown how additional improvement in the results for yttria can be obtained by applying an infinite thickness correction to the fused disk specimens and controlling the sample-to-flux ratio.

EXPERIMENTAL SECTION

Preparation of Oxide Mixtures. Cerium dioxide and yttrium oxide powders (99.99% pure, purchased from Research Chemicals Division, NUCOR Corp., Phoenix, AZ) were ignited to 1000 °C for several hours. These powders were characterized by scanning electron microscopy. The mean particle size was 24 μm for CeO_2 and 16 μm for Y_2O_3 . To prepare powder compositions with various CeO_2/Y_2O_3 ratios, the pure oxides were weighed to yield a total mixture weight of 60 to 90 g. The powders were each placed in ethanol in a blender and the slurries mixed for several minutes, dried, heated to 800 °C overnight, and stored in a desiccator.

Fusion of Oxide Mixtures. Lithium tetraborate (Spex Industries) was heated to 500 °C for 2 h and then stored in a desiccator. Two series of fused samples were prepared in which the sample to flux ratio was held constant, that is 0.35 g of oxide plus 6.2 g of flux (CY samples), or varied from 0.06 to 0.37 of oxide plus 6.0 g of flux (YC samples). The CY samples were prepared by adding known amounts of the individual dried oxide powders to the flux and then fused. The YC samples were prepared by adding premixed oxide powders as described above to the flux and fused. Fusions of the flux-oxide mixtures were performed at 1100 °C from 20 to 40 min in an automated fusion device previously described (9). The bottom surfaces of the resultant fused disks were ground flat and polished. Standards were

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Table II. Analysis of CeO₂-Y₂O₃ Mixtures with Different Sample/Flux Ratios^a

sample	% CeO ₂ present	% CeO ₂ found	% Y ₂ O ₃ present	% Y ₂ O ₃ found ^b	% rel error ^b	% Y ₂ O ₃ found ^c	% rel error ^c	sample/flux	actual disk thickness, mm	calcd infinite thickness, mm
YC101	92.38	91.49	7.62	8.84	16.0	7.93	4.1	0.0621	2.3	3.2
YC201	83.73	84.13	16.27	17.41	7.0	16.34	0.4	0.0312	2.3	5.4
YC401	72.75	72.70	27.25	25.14	-7.7	26.61	-2.4	0.0140	2.3	8.5
YC504	61.52	62.03	38.45	32.96	-14.2	37.58	-2.3	0.0104	2.1	9.7
YC301 (std)	76.70		23.30		11% ^d		2.3% ^d	0.0190	2.4	7.4

^a Use one standard (YC301) for calibration. W tube, 60 kV. ^b No infinite thickness correction and corresponding relative error. ^c With infinite thickness correction and corresponding relative error. ^d Average relative error.

prepared in an identical manner as the CY samples, fused, and polished as described above. The area of the disk exposed to x-radiation for analysis was 7.1 cm². The thickness of the disk samples was measured at various points along the diameter with a digital linear gauge and the average thickness of each disk calculated. The variability of the disk thickness across the diameter was about $\pm 10\%$.

X-ray Analysis. X-ray measurements were performed with a Philips AXS automated sequential X-ray spectrometer with a tungsten target X-ray tube operated at 60 kV. The Y K α line was measured using a LiF (220) crystal at a 2θ angle of 33.76° , and at a 2θ of 34.40° for background. The Ce L α line was measured at a 2θ of 128.26° , and 130.40° for background. The proportional and scintillation detectors were operated in tandem.

RESULTS AND DISCUSSION

Quantitative analysis of fused specimens of rare-earth and lanthanide compounds can be performed in several ways depending on how the analyst prefers to handle the X-ray absorption effects in these specimens. A heavy absorber can be added prior to fusion to obtain a linear dependence of X-ray analyte intensity vs. composition. Similarly, an internal standard can be found with an appropriate noninterfering X-ray line energy which could be fused along with the oxide mixture. Although both methods are valid in principle, we found that in practice, direct correction of interelement effects is preferable if appropriate standard samples can be prepared. A major consideration in the choice of heavy absorber or internal standard is that it must dissolve homogeneously in the fusion preparation. A comparison of advantages and disadvantages of heavy absorbers vs. interelement correction via digital computation has been discussed in some of our earlier work (9).

So-called fundamental parameter computer programs for correction of interelement effects are finding increased use especially in X-ray laboratories which analyze samples of varying matrix composition. Such methods are preferred especially in situations where only a limited number of standard reference materials are available. The fundamental parameter program NRLXRF was used in the present work for correction of absorption effects.

In choosing the analyte X-ray lines to be measured, the analyst has a choice of either the K α or L α line for yttrium. The Y L α is of relatively low energy (1.92 keV) and strongly absorbed by the matrix, whereas the Y K α is more energetic (14.93 keV) and more desirable for the measurement of low concentrations. A problem encountered, however, is that the fused disk may not meet the infinitely thick criteria because of the Y K α line energy. This can lead to a systematic error if the analyte samples and standards are not closely matched in composition. For disks of thickness t (cm), the yttrium X-ray intensity, I_t , can be corrected using

$$\frac{I_t}{1 - \exp[-(\mu/\rho)\rho t]} = I_\infty \quad (1)$$

where I_∞ is the yttrium X-ray intensity corresponding to a disk of infinite thickness, μ/ρ is the mass absorption coefficient of the specimen (cm²/g), ρ is the density of oxide constituents in the specimen (g/cm³), and

$$\overline{\mu/\rho} = (\mu/\rho)_{\lambda_{\text{pri}}} \csc \phi + (\mu/\rho)_{\lambda_{\text{L}}} \csc \psi$$

where λ_{pri} and λ_{L} are the primary and analyte-line wavelengths and ϕ and ψ are the corresponding X-ray angles of incidence and emergence, respectively. Infinite thickness is defined where $I_t/I_\infty = 1$.

For standard samples corrected intensities are obtained directly from eq 1 and entered in NRLXRF. Successive approximations are made for analyte specimens where I_t is first entered in NRLXRF to give an initial estimate of composition. Further estimates are made using corrected intensities where after three iterations the final results are obtained.

In Table I are summarized results using two standards for calibration chosen at the extremes of the composition range. The sample-to-flux ratio was held constant and the average relative error was reduced almost 2-fold after thickness correction.

It is also important to control the sample-to-flux ratio in fusions where infinite thickness criteria are not met. In the series shown in Table II, one standard was used to analyze samples of various sample-to-flux ratios. Here, the calculated infinite thicknesses for each sample as well as the standard are quite different. Correction results in about a 5-fold improvement in accuracy for yttrium.

In conclusion, quantitative XRF analysis of ceria-yttria mixtures can be performed conveniently using automated borate fusion with relative errors less than 1% for major concentrations. It is important to keep the sample-to-flux ratio constant for both standards and samples, and corrections for infinite thickness should be considered, if analyte X-ray lines above 8 keV are measured. A FORTRAN computer program (SDCC) to correct for infinite thickness is available from the authors upon request.

Registry No. CeO₂, 1306-38-3; Y₂O₃, 1314-36-9; Li₂B₄O₇, 12007-60-2.

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terials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation of endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Detection of Organophosphorus Compounds with a Coated Piezoelectric Crystal

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Piezoelectric quartz crystals coated with PVP-TMEDA and PVBC-TMEDA were found to be sensitive to DIMP in the parts-per-billion concentration range. These coatings have outstanding advantages compared to those previously described: higher sensitivity, faster response, and longer life-time. In addition, the calibration curves pass through the origin, and the reproducibility and base line stability are within ± 2 Hz. Also, the response and recovery times are on the order of minutes for the PVP-TMEDA coating and on the order of seconds for the PVBC-TMEDA copper complex. No serious interferences were observed.

The oscillating quartz piezoelectric crystal was first described for use as an analytical device by King (1). In this technique a coating specific for detection of one compound (i.e., organophosphorus compounds) is placed on the electrode surface of the quartz crystal. If interaction occurs, the presence of the compound is indicated; the magnitude of the frequency change quantifies the amount of compound present, according to the Sauerbrey equation

$$\Delta F = -k \Delta m$$

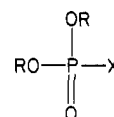
where Δm is the amount of substance adsorbed onto the crystal.

Research for new coatings sensitive to organophosphorus compounds is of great practical importance, especially for compounds developed for chemical warfare (CW) applications. The optimization of coating sensitivity and selectivity toward the highly toxic cholinesterase inhibitory organophosphorus pesticides and CW agents is of interest to many scientists.

Previously, we devoted many efforts to the development of a piezoelectric crystal detector for organophosphorus compounds in air. The ferric chloride (FeCl_3) complex of pesticides and the cobalt (Co) complex of isocyanobenzoylacetate (IBA) were used as adsorptive coatings (2, 3). The FeCl_3 complex showed a very slow response and lacked the desired sensitivity. The application of the IBA coating was limited by a very short lifetime.

A ternary mixture coating of 1-*n*-dodecyl-3-(hydroximinomethyl)pyridinium iodide (3-PAD), Triton X-100, and sodium hydroxide (NaOH) was reported to have faster response, longer lifetime, and higher sensitivity for the parts-per-million (ppm) range (4-6). Diisopropyl methylphosphonate (DIMP) was used as a model compound for detection and assay of

organophosphorus compounds with the G-agent structure (pentavalent phosphorate with an active leaving group, X



Additionally, L-histidine hydrochloride was also reported as an excellent coating for assay of organophosphorus compounds of the malathion type (4-6). Guilbault and Kristoff used uncoated crystals for the detection of organophosphorus vapors (7).

Several papers suggest the use of copper complexes for hydrolysis of phosphorus esters (8, 11). In this application, copper is complexed, and ligands containing basic nitrogen are used. The reaction takes place in two steps: first, the copper complex binds the phosphorus ester reversibly; second, the adduct-product formed is irreversibly broken down by hydrolysis. This second reaction is unlikely to occur on a copper complex used as a coating for the crystal.

From a practical viewpoint, the copper complexes of importance have a fast, reversible, and weak complexation toward organophosphorus compounds at ambient temperature. Indeed, copper complexes have already been evaluated for the detection of organophosphorus compounds in air (12, 13).

In this study, two types of copper(II) chelates were investigated. (Tetramethylethylenediamine)copper(II) chloride (TMEDA) was connected to hydrophilic poly(vinylpyrrolidone) (PVP), and to hydrophobic poly(vinylbenzyl chloride) (PVBC) polymers. Thus, PVP-TMEDA polymer-bonded chelates were synthesized and evaluated.

EXPERIMENTAL SECTION

Instrumentation. A schematic diagram of the experimental instrumentation is shown in ref 7. Nitrogen gas flowed through a drier reservoir filled with phosphorus pentoxide (P_2O_5) mixed with glass rings. The gas flow was divided into three parts: F_1 is the flow stream for desorption; F_2 , for dilution; and F_3 , for generation. At all times $F_1 = F_2 + F_3$. The required concentration of DIMP in the gas flow was adjusted by varying the (F_2/F_3) ratio. In this work, the temperature was kept constant by a water bath, and the gas flow rates were varied. The flow rate of the gas entering the detector cell was 100 cm^3/min . The cell design was essentially the same as that described earlier (14). The gas stream was focused on both faces of the coated crystal. A four-port valve was used to make a selection between either pure nitrogen or the carrier gas containing DIMP. An injection port was inserted into