ability agrees with the variability of the method for the standard benzoic acid samples which contained the same level of acid. Therefore, this correlation shows that polymeric acids can be titrated successfully with the same degree of precision and accuracy as benzoic acid.

Since the ionic strength is relatively constant during the titration and these polymer fractions provide a broad range of molecular weights, the effects of increases in molecular weight on the shape of the titration curves were investigated. Figure 4 shows typical potentiometric titration curves (recorded manually) for a constant molecular weight (fraction 1) with varying sample size. The HNP (± 10 mV) is independent of sample size (0.5 to 8.0 mg of copolymer). Figure 5 shows the potentiometric titration curves that were recorded manually using a constant sample size and varying molecular weight. Curves D, E, and F are typical for samples with number-average molecular weights of 135,000, 72,000 (unfractionated sample), and 20,000, respectively. These curves show that the sharpest inflection and most positive half-neutralization potentials are obtained for the highest-molecular-weight samples. In fact, the difference between the HNP of the highest-mo-

lecular-weight (Curve D) and the lowest-molecular-weight (Curve F) samples is about 50 mV, far outside the ± 10-mV error expected for such titrations. Since the HNP is a measure of the apparent ionization constant, these data suggest that K_a increases with molecular weight. This could possibly be explained by changes in nearest-neighbor interactions (17) with configurational changes among the polymer fractions.

ACKNOWLEDGMENT

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Determination of Trace Elements in Silicate Matrices by Differential Cathode Ray Polarography

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Methods are described for the analysis of some new Trace Elements in Glass Standard Reference Materials by differential cathode ray polarography. Iron and titanium were determined in the 500-, 50-, 1-, 0.02-ppm and base glasses after cupferron and ammonium hydroxide separations. Nickel was determined in the 500- and 1-ppm samples after extraction with dimethylglyoxime.

During the past few years there has been an increasing need for new Standard Reference Materials especially in the field of trace analysis. There has been a particular demand for standards of glassy or rock-like materials certified for a large number of elements in several ranges of trace concentrations.

To meet these needs, the National Bureau of Standards has issued four new glass standards, each containing 61 added elements at the 500-, 50- 1-, and 0.02-ppm level, respectively. These glasses were prepared at Corning Glass Works, Corning, N.Y., under carefully controlled conditions. The undoped material was prepared from extremely pure starting materials; its composition and the added elements are shown in Figure 1.

The analysis of any material to which 61 different elements have been added obviously poses some very interesting as well as challenging problems to any analytical technique. Polarography, because of its sensitivity, resolution, and relatively inexpensive instrumentation, should be a highly advantageous technique for many of these determinations. Unfortunately, polarography seems to have

fallen into disfavor in this country; in fact, it has never achieved wide-spread acceptance in the field of glass, mineral, and rock analysis. A cursory survey of the literature showed few applications of polarographic methods of analysis of these materials.

It is difficult to understand why this useful analytical tool has not been more routinely used. Work at the National Bureau of Standards over the past few years with differential cathode ray polarography has shown its utility through analyses of matrices such as air particulates, waste water, high purity materials, ores, botanicals, and alloys (1–4). The differential technique potentially allows coverage of concentrations from ppb-amounts to major constituent levels. This range far exceeds the capabilities of most other analytical techniques. Its accuracy and reliability have also been proved by comparisons of results on the same material with other techniques, such as isotope-dilution mass spectrometry and atomic absorption.

Most of the added elements could be determined polarographically, in fact over 20 of those added have been determined in this laboratory in the matrices just listed. Many of the determinations were done directly with no separations. For the analysis of the glasses, however, with the known presence of 61 possible interferences, separations were necessary.

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TRACE ELEMENT GLASSES

Figure 1. Elements added to Trace Elements in Glass Standard Reference Materials

Interferences and Blanks. Although the cathode ray polarograph is sufficiently sensitive to measure as little as a nanogram of some elements, the practical limit is often raised to the microgram level for such elements as lead, iron, aluminum, copper, etc. because of the large blanks involved. The blank arises from two main sources, the environment and the reagents used in chemical processing. Using the differential cathode ray polarograph, the blank is generally measured in the second cell and its signal is electrically subtracted from that of the sample contained in the first cell.

Of the three elements determined in the glasses—iron, titanium and nickel—the greatest total blank problems were found with iron. Prior to the beginning of this work, blanks of about 2 to 3 μg of iron and 0.3 μg of titanium were usually obtained. In one instance, a blank of 13 μg of iron was found. These experiments were performed, however, in a room where extensive corrosion of the metal cabinets and walls had occurred as a result of chemical operations. When the experiments were performed in another laboratory where corrosion had not occurred, the blank was lowered to 0.5 μg for iron, and titanium was not detected.

To lower the blank coming from the environment, laminar-flow class-100 clean hoods were installed in the laboratory. To determine the blank actually coming from the atmosphere into the sample container during processing, empty 50-ml breakers were allowed to stand in the clean hood and in the regular laboratory hood (in the uncorroded room) for 6 days. Values for the atmosphere blank of about 0.02 μg of iron in the clean hood and about 0.04 μg of iron in the regular laboratory hood were obtained for the 6-day period. The blank obtained in the clean hood should also be more reproducible because, in the regular laboratory hood, occasional gross contamination may occur.

A considerable portion of the total blank comes from reagents. Whenever possible, specially purified reagents are used for all trace analytical problems. A number of commercially purified reagents were analyzed to determine their suitability for use. Results obtained for iron in reagents from one supplier were: HCl, 11 ppb; HNO₃, 6 ppb; HClO₄, 2 ppb; and HF, 9 ppb; while results from another source were HCl, 16 ppb; HNO₃, 52 ppb; and

HClO₄, 28 ppb. Although one lot of nitric acid and one of perchloric acid were rather high in iron, the rest were acceptable for the determination of iron at the 10-ppm level or greater. For amounts of iron less than 1 ppm, however, much purer reagents are needed and are now being prepared in the NBS Analytical Mass Spectrometry Section by sub-boiling distillation in quartz stills (5).

It was then necessary to find the optimum supporting electrolytes for the elements in question. It seemed probable that both iron and titanium could be determined simultaneously, since an EDTA–sodium acetate supporting electrolyte had been used previously in this laboratory for titanium with good results, and tables of half-wave potentials showed the iron reduction peak to be about 0.3 V separated from that of titanium, which would be more than sufficient to allow measurement of both. A similar separation of reduction peaks was reported for a sodium pyrophosphate–sulfuric acid supporting electrolyte (6). Standard curves were then checked for both supporting electrolytes in the 1- to 10-ppm concentration range in the final solution. The EDTA–sodium acetate media gave a slightly more linear calibration curve than that of pyrophosphate. In the low concentration ranges, the pyrophosphate supporting electrolyte gave somewhat greater sensitivity than EDTA–sodium acetate. An oxalic acid supporting electrolyte used previously in the determination of small amounts of iron in air particulates (2) could also be used.

Possible interferences in the doped glass such as uranium, copper, molybdenum, etc. could be removed by ammonium hydroxide and cupferron separations. Titanium and iron, as well as niobium, tantalum, zirconium, copper, vanadium, molybdenum, tungsten, bismuth, and a few others would be precipitated or extracted with cupferron. Iron and titanium as well as niobium, tantalum, and zirconium, could then be separated from vanadium, molybdenum, copper, tungsten, etc. by precipitation with ammonium hydroxide.

To check the proposed scheme of analysis, these separations were applied to SRM 80, a soda lime glass which is now out of stock. One-gram samples of SRM 80 were dis-

(5) E. C. Kuehner, R. Alvarez, P. J. Paulsen, and T. J. Murphy, *Anal. Chem.*, **44**, 2050 (1972).
(6) S. Kumar and B. C. Sinha, *Glass Ceram Bull.*, **5**, 18 (1958).

Table I. Iron and Titanium in Soda Lima Glass, SRM 80

		% Fe by polarography	
Recommended value		Procedure A	Procedure B
0.039% Fe	average	0.0381	0.0365
		$\sigma = 0.0002$	0.0003
		% Ti by polarography	
Certified value		Procedure A	Procedure B
0.014% Ti	average	0.0138	0.0138
		$\sigma = 0.0002$	0.0003

solved with hydrofluoric and perchloric acids along with solutions for a calibration curve to which a small amount of zirconium solution was added as a carrier. Hydrofluoric acid was volatilized, ammonium hydroxide and cupferron separations were made, organic material was destroyed, and the solutions were diluted to 25.0 ml. Duplicate 10.0-ml aliquots were then taken in order to check further both supporting electrolytes. The results for iron and titanium are shown in Table I.

Procedure A used a supporting electrolyte of EDTA-sodium acetate and procedure B, pyrophosphate. The results show good agreement with the recommended values in both supporting electrolytes.

The ammonium hydroxide separation could probably be omitted for the 0.02- and 1-ppm glasses since the iron and titanium level was assumed to be sufficiently higher than that of the copper, molybdenum, etc. which would also be extracted with cupferron. For nickel, previous experience has shown that pyridine–pyridinium chloride or –pyridinium sulfate supporting electrolytes are suitable for its determination with few direct interferences. Aluminum, iron, and some of the other ions present in the glasses, however, might form a colloidal precipitate occluding some nickel, making separation advisable for most accurate results. Dimethylglyoxime is an excellent extractant for nickel under appropriate conditions with only slight traces of copper, cobalt, and iron being extracted. None of these in trace amounts would be an interference in the pyridine supporting electrolyte. The precipitation of iron hydroxide at the pH required for the extraction of the nickel dimethylglyoxime complex can be prevented by the addition of tartrate or citrate. The nickel extraction is reported to be incomplete at times in the presence of excess manganese (7), but this effect can be eliminated by addition of hydroxylamine hydrochloride.
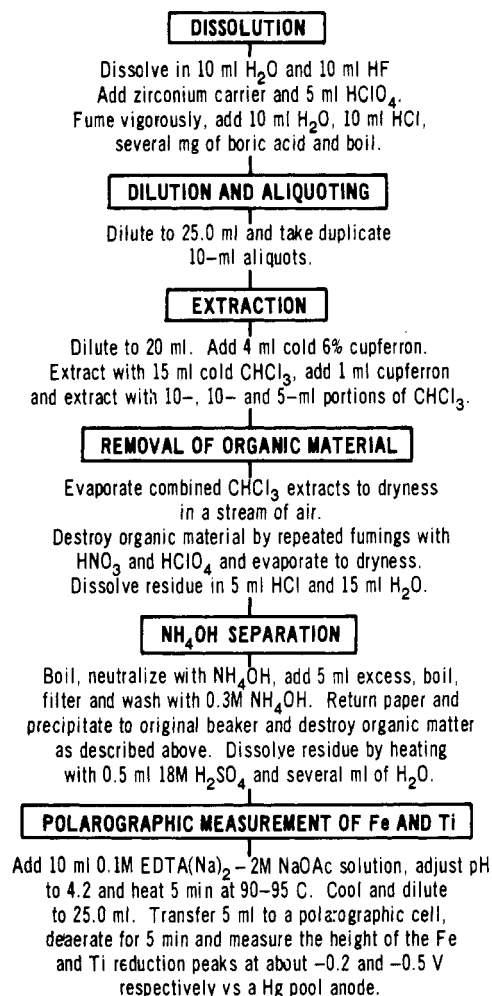
Since the standard soda lime and borosilicate glasses were not certified for nickel, but probably contained a measurable amount, the procedure was checked by spiking solutions of 1-gram portions of SRM 80 with 50- to 500-μg portions of nickel. The solutions of the unspiked glass could then be used as a blank in the second cell when the final differential polarographic measurement was made, or could be measured against a reagent blank in the second cell and subtracted from the spiked values. Average recoveries of 101% were obtained.

For this method to be applicable for the analysis of the 1-ppm glass, it was necessary to scale down the volumes. By extracting from volumes of less than 10 ml, 0.5 μg of nickel was quantitatively recovered.

EXPERIMENTAL

Apparatus. A Davis Differential Cathode Ray Polarotrace manufactured by Shandon Southern, Camberley, Surrey, England was used for all the determinations in the twin cell, subtractive mode of operation.

(7) W. Oelschläger, *Z. Anal. Chem.*, **146**, 339 (1955).

DISSOLUTION

Dissolve in 10 ml H_2O and 10 ml HF
Add zirconium carrier and 5 ml $HClO_4$.
Fume vigorously, add 10 ml H_2O, 10 ml HCl,
several mg of boric acid and boil.

DILUTION AND ALIQUOTING

Dilute to 25.0 ml and take duplicate
10-ml aliquots.

EXTRACTION

Dilute to 20 ml. Add 4 ml cold 6% cupferron.
Extract with 15 ml cold $CHCl_3$, add 1 ml cupferron
and extract with 10-, 10- and 5-ml portions of $CHCl_3$.

REMOVAL OF ORGANIC MATERIAL

Evaporate combined $CHCl_3$ extracts to dryness
in a stream of air.
Destroy organic material by repeated fumings with
HNO_3 and $HClO_4$ and evaporate to dryness.
Dissolve residue in 5 ml HCl and 15 ml H_2O.

NH_4OH SEPARATION

Boil, neutralize with NH_4OH, add 5 ml excess, boil,
filter and wash with 0.3M NH_4OH. Return paper and
precipitate to original beaker and destroy organic matter
as described above. Dissolve residue by heating
with 0.5 ml 18M H_2SO_4 and several ml of H_2O.

POLAROGRAPHIC MEASUREMENT OF Fe AND Ti

Add 10 ml 0.1M $EDTA(Na)_2 - 2M$ NaOAc solution, adjust pH
to 4.2 and heat 5 min at 90–95 C. Cool and dilute
to 25.0 ml. Transfer 5 ml to a polarographic cell,
deaerate for 5 min and measure the height of the Fe
and Ti reduction peaks at about -0.2 and -0.5 V
respectively vs a Hg pool anode.

Figure 2. Determination of iron and titanium in 500-ppm glass'

Procedure. *Iron and Titanium in 500-ppm Glass.* Clean the 1-gram wafers first with alcohol, then with warm 6M hydrochloric acid. Rinse, dry, and weigh into Teflon beakers covered with Teflon lids. Proceed as directed in Figure 2. Measure all solutions subtractively with a differential cathode ray polarograph against a blank carried through each step of the procedure. A calibration curve is prepared from solutions of high purity iron and titanium. These solutions are also taken through each step of the procedure.

Iron and Titanium in 50-ppm Glass. The same procedure is used as for the 500-ppm glass, except the entire solution of the 1-gram wafer is analyzed, and the supporting electrolyte consists of 0.4 ml of 18M sulfuric acid, 5 ml of EDTA–sodium acetate solution, and the final dilution is to 10.0 ml.

Iron and Titanium in 1-ppm Glass. The same procedure is used as for the 50-ppm glass, except the ammonium hydroxide separation is omitted, and 2 ml and 0.5 ml of 6% cupferron is used for the extractions. The supporting electrolyte contains 0.2 ml of 18M sulfuric acid, 0.5 ml of saturated sodium pyrophosphate, and ammonium hydroxide to bring the pH to 2. Deaerate the solutions at least 10 minutes prior to polarographic measurements.

Iron and Titanium in 0.02-ppm Glass. The same procedure is used as for the 1-ppm glass, except the supporting electrolyte consists of 0.8 ml of 18M sulfuric acid, 4 ml 0.25M oxalic acid, and ammonium hydroxide to bring the pH to 2 and a final dilution volume of 10.0 ml.

Nickel in 500-ppm Glass. Clean the 1-gram wafers in alcohol, followed by dilute nitric acid, then dissolve and fume as already described for iron and titanium. Dilute with water, transfer to a separatory funnel and dilute to 50 ml. Add 5 ml of a 10% sodium citrate solution and 2 ml of a 10% hydroxylamine hydrochloride solution. Make just basic with 7.5M ammonium hydroxide and add 0.5 ml in excess. Add 5 ml of filtered 1% dimethylglyoxime in alcohol, mix and extract for 1 minute each with 20-, 15-, and 10-ml portions of chloroform, combining the extracts. Evaporate to dryness and destroy the organic material as described for iron

Table II. Polarographic Determination of Iron in Doped Glass

Sample, ppm	Average, ppm	σ, ppm
500	460	10
50	51.3	0.8
1	13.5	0.7
0.02	11.0	0.8

Table III. Polarographic Determination of Titanium in Doped Glasses

Sample, ppm	Average, ppm	σ, ppm
500	434	10
50	50.0	0.3
1	3.1	0.2
0.02	2.5	0.2

Table IV. Polarographic Determination of Nickel in Doped Glasses

Sample, ppm	Average, ppm	σ, ppm
500	450	7
1	0.95	0.08

and titanium. Add 1 ml of $6M$ hydrochloric acid and a few drops of SO_2 water to reduce any residual chromium and evaporate to dryness. Dissolve the residue in 0.3 ml of $18M$ sulfuric acid by heating gently. Add 1.5 ml of pyridine, dilute to 25.0 ml, and deaerate 5 minutes. Measure the nickel reduction peak at about -0.9 V vs. a mercury pool anode. Measure all solutions subtractively against a blank which has been carried through each step of the procedure. Solutions for the calibration curve which contain similar amounts of nickel are also taken through each step of the procedure.

Nickel in 1-ppm Glass. Nickel is determined by essentially the same procedure as for the 500-ppm glass, except the volumes of all reagents used are reduced. The volume of the aqueous layer during the extraction is not greater than 8 to 10 ml and the final volume of the supporting electrolyte is 5.0 ml.

RESULTS AND DISCUSSION

Some difficulty was experienced with the 500-ppm glass in keeping titanium in solution at various steps of the procedure. After fuming with perchloric acid to remove the hydrofluoric acid, a large amount of insoluble residue was obtained, probably consisting of calcium and rare earth fluorides, etc. Prolonged fuming to convert the fluorides to perchlorates also results in the hydrolysis of titanium, niobium, tantalum, tungsten, etc. Addition of hydrochloric acid was necessary to redissolve the hydrolyzed materials. Concentrated sulfuric acid is a better solvent for titania, but the excessive precipitation of calcium and lead sulfates would preclude its use at this stage. Reversing the order of separations and precipitating with ammonium hydroxide before extraction with cupferron was unsuccessful, because the bulky precipitate resulting from the presence of almost every member of the ammonium hydroxide group, including the rare earths, made thorough washing of the precipitate very difficult. Some problems were also experienced with obtaining completely clear solutions in the sodium pyrophosphate supporting electrolyte, so it was not used in the final determination for the 500-ppm glass.

To determine if any deviations result from sample inhomogeneity or arise from the procedure, duplicate aliquots are taken. Some errors from loss or contamination could, of course, occur during dissolution and before the aliquots were taken; but the bulk of the chemical processing occurs after the aliquoting.

While the agreement between aliquots was somewhat better than that between separate samples, it was not significantly better to show conclusively that sample inhomogeneities exist. The average results for iron and titanium are shown in Tables II and III, respectively. An average value of 461 ppm of iron was obtained by spectrophotometric analyses (R. W. Burke and E. R. Deardorff, Analytical Coordination Chemistry Section, Analytical Chemistry Division, National Bureau of Standards) which is in excellent agreement with the polarographic results. No other values have been reported for titanium as yet. In taking pure solutions of iron and titanium with zirconium added as carrier through the entire procedure, recoveries of 99.6% of the iron and 99.4% of the titanium were obtained.

Niobium and tantalum which had been added to the glasses could probably have been determined at the same time, as they are also separated with the iron and titanium. Their reduction peaks follow that of titanium and are sufficiently separated for good resolution.

The results for iron and titanium in the 50-ppm glass are shown in Tables II and III.

For the 1-ppm glass, the ammonium hydroxide separation was omitted on the first set, since the base iron and titanium levels were expected to be sufficiently higher than those of copper, molybdenum, etc. which would also be extracted with cupferron. The results are also shown in Tables II and III.

Very careful deaeration was required for these samples, prior to polarographic measurement, as the presence of oxygen at these high instrumental sensitivities distorts the base line and makes reproducible measurements difficult. The levels of copper and several other possible interferences were found to be higher than originally expected, so another set was taken through the entire procedure, including the ammonium hydroxide separation. The average of 13.3 ppm of iron found is in good agreement with the value of 13.5 shown in Table II obtained without the ammonium hydroxide separation, and the standard deviation (0.48 ppm) has been somewhat improved.

The ammonium hydroxide separation was omitted in the analysis of the 0.02-ppm glass, since the interference level would be even lower than for the 1-ppm standard.

Iron and titanium were determined in the undoped glass by the same procedure and values of 12.7 ± 0.5 ppm of iron and 2.8 ± 0.2 ppm of titanium were obtained.

It is seen by comparison with Tables II and III that the results are higher for the undoped glass than for the 0.02-ppm glass. These results were the first reported on these two samples and at first it was thought that the two samples had been somehow interchanged. However, when results for some of the other common elements, such as copper, were reported, the same apparent reversal persisted. It was then speculated that the undoped glass, which had been prepared first, had cleaned the walls of the melter of certain impurities and hence became contaminated. The undoped glass is not being issued as a Standard Reference Material.

The results for nickel in the 500-ppm glass are shown in Table IV. The results are in excellent agreement with the 451-ppm value obtained by spectrophotometry (R. W. Burke and E. R. Deardorff, Analytical Coordination Chemistry Section, Analytical Chemistry Division, National Bureau of Standards) and in relatively good agreement with the 458.7 ppm obtained by isotope-dilution mass spectrometry (I. L. Barnes, E. Garner, and L. A. Machlan, Analytical Mass Spectrometry Section, Analytical Chemistry Division, National Bureau of Standards).

The results for nickel in the 1-ppm glass are also shown in Table IV. The agreement between duplicates of the same sample position was somewhat better than between different positions, but again the difference was not great enough to establish sample inhomogeneity.

The determination of nickel in the 50-ppm glass has not yet been started, but with a reduced extraction volume, accuracies as good or better than that obtained for the 500-ppm sample are expected. Also, by the use of smaller extraction volumes, better results could probably be obtained on the 500-ppm standard.

The polarographic determination of a number of other elements is of considerable interest. A method currently under investigation for the simultaneous determination of bismuth, copper, lead, thallium, cadmium, and zinc in another matrix is also applicable to all of the trace glass standards. The accuracy attained will probably not be as great as that by isotope-dilution thermal ionization mass spectrometry, but should certainly be comparable to or better than most other techniques. These standards have now been certified for 43 elemental concentrations covering 13 different elements. Data are also given in the certificates for the concentrations of 30 other different elements in the four standards (8).

These standards are also ideally suited for the development of new and improved analytical methods for most elements in many matrices. The bulk of the glass matrix can be easily removed by fuming with hydrofluoric acid.

The desired matrix may then be added to the remaining portion in the form of a high purity material, thus synthesizing a sample which can represent most inorganic analytical situations. In addition, these standards were initially used in the development of the polarographic methods for the analysis of iron, titanium, and nickel in Apollo 14 lunar samples (9). However, since the iron and titanium levels in the lunar rocks analyzed were significantly higher than in the glass matrices, a number of procedural modifications were used for the lunar analyses which were developed using U.S. Geological Survey andesite AGV-1 (10).

This work has conclusively demonstrated the applicability of polarography to these types of problems. Although a number of other analytical techniques, including atomic absorption, flame photometry, neutron activation, mass spectrometry, and spectrophotometry were involved in the glass analyses, only polarography is potentially applicable to the entire range of concentrations encountered in these matrices.

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Rapid Macrodetermination of Oxygen in Uranium Oxides by Graphite Reduction

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The need for a fast direct method of determining oxygen in metal–oxide nuclear fuels, by which simpler indirect methods may be checked, is met by a modification of the graphite-reduction method. Using a newly designed reaction chamber, the oxygen of 0.1-gram samples of uranium oxide is converted quantitatively to CO in less than 10 minutes by heating in a sealed graphite capsule at 2400 °C and directing the effluent carrier gas stream through a bed of graphite chips at $\sim$2400 °C. The graphite capsule is remotely manipulated into and out of the graphite furnace without opening the reaction chamber. The CO is oxidized to CO_2 and measured in a high capacity capillary manometer. The relative error in the oxygen data is about 0.2%. The analysis of a weighed encapsulated sample can be completed in one-half hour.

The oxygen-to-metal ratio, O/M, is a significant parameter in metal–oxide nuclear fuel technology. It is relatable to the chemical reactivity of the fuel with cladding materials in which it is contained and with fission products that continuously form within the fuel as a result of burnup. The O/M ratio is also relatable to physical changes

that accompany burnup, such as changes in thermal conductivity, ceramic strength, and melting points (1). Consequently, the determination of the O/M ratio of oxide fuels is important to the design and operation of modern nuclear power reactors.

Several methods, both direct and indirect, have been applied in the determination of either total oxygen or O/M ratio in uranium oxides and in uranium–plutonium oxide mixtures. The indirect methods, other than the estimation of oxygen by subtracting all other measured components from 100%, are variously based on gas–solid interactions, aqueous reactions, or changes in physical properties. Direct methods are based on the measurement of a gas that is derived directly from the oxygen of the oxide.

Indirect methods, some of which afford excellent precision with relatively simple equipment, are further based on assumptions that certain relationships between measurable chemical or physical changes and the oxygen content of the oxide are valid and reliable. Because of these assumptions, indirect methods are usually more applicable to the measurement of small O/M variations in metal oxygen systems than to the quantitative determination of

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