MCC

Materials Characterization Center

Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials

Summary Report

June 1981

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MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON COMPOSITIONAL AND MICRO-
STRUCTURAL ANALYSIS OF NUCLEAR WASTE
MATERIALS

SUMMARY REPORT

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MATERIALS CHARACTERIZATION CENTER WORKSHOP ON
COMPOSITIONAL AND MICROSTRUCTURAL ANALYSIS OF
NUCLEAR WASTE MATERIALS

SUMMARY AND CONCLUSIONS

The purpose of the Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials, conducted November 11 and 12, 1980, was to critically examine and evaluate the various methods currently used to study non-radioactive, simulated, nuclear waste-form performance. Workshop participants recognized that most of the Materials Characterization Center (MCC) test data for inclusion in the Nuclear Waste Materials Handbook will result from application of appropriate analytical procedures to waste-package materials or to the products of performance tests. Therefore, the analytical methods must be reliable and of known accuracy and precision, and results must be directly comparable with those from other laboratories and from other nuclear waste materials.

The 41 participants representing 18 laboratories in the United States and Canada were organized into three working groups: "Analysis of Liquids and Solutions", "Quantitative Analysis of Solids", and "Phase and Microstructure Analysis". Each group identified the analytical methods favored by their respective laboratories, discussed areas needing attention, listed standards and reference materials currently used, and recommended means of verifying interlaboratory comparability of data.

The following major conclusions were reached:

- 1) An analytical round robin using reference specimens should be conducted prior to (or at least concurrent with) any MCC leach-test round-robin series. The initial results of the analytical round robin are expected to reveal any significant discrepancies in procedures and provide information regarding relative precision, detection limits, and data bias resulting from analytical practices, independent of specific applications to MCC tests.

- 2) None of the available certified reference materials is entirely suitable for verification of nuclear waste material analytical procedures. Several National Bureau of Standards (NBS) glass, refractory and general standard reference materials are available for checking basic methods, and should be used by participating laboratories until specific standards become available.
- 3) Insufficient attention is being given by most individual laboratories to evaluation of the statistical significance of analytical data (precision, bias, detection limits, and accuracy). Definitions and methods of calculations of statistical significance are inconsistent among the laboratories. Test data reports should always include information on statistical significance of data in sufficient detail to permit evaluation by the reader.
- 4) All analytical data reported for MCC materials evaluations should include current reports of analyses of the best available reference material or standard, preferably traceable back to an NBS or other certified reference, for assurance of analytical methods control. Reports should also include statements of expected analytical precision for each element reported, based on previous experience in that laboratory.
- 5) The analytical methods most commonly used by the workshop participants are
 - Solutions--Plasma-excitation emission spectroscopy; atomic absorption spectroscopy; neutron activation analysis.
 - Solids--Neutron activation analysis; X-ray fluorescence spectroscopy; near-surface spectroscopy methods; sample dissolution + solution analysis.
 - Phases--X-ray diffraction; infrared reflection spectroscopy; microprobe analyses; microscopy and image analysis; scanning calorimetry.

- 6) Surface analysis methods, including near-surface studies (within ~50 Å of the exposed surface) are increasingly important in predicting long-term behavior of highly stable waste forms. Quantitative interpretation of observations by secondary ion mass spectroscopy (SIMS), Auger, etc. needs to be improved.
- 7) Detailed specification of explicit analytical methods to be used in providing data for MCC use is neither practical nor desirable. Instead, diverse methods must demonstrate similar results when applied to similar reference materials. This approach will provide increased confidence in reliability of all data, and permit each laboratory to capitalize on its own previous experience, current expertise of its staff members, and its existing capital equipment investment.

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GLOSSARY

AA	atomic absorption
AES	Auger electron spectroscopy
DCP	direct-current plasma
DTA	differential thermal analysis
EDX	energy dispersive X-ray fluorescence analysis
FTIR	Fourier-transform infrared
ICP	inductively coupled plasma
IRRS	infrared reflection spectroscopy
NAA	neutron activation analysis
NMS	nuclear microprobe spectroscopy
RBS	Rutherford backscattering spectroscopy
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

WORKSHOP ON COMPOSITIONAL AND MICROSTRUCTURAL ANALYSIS OF NUCLEAR WASTE MATERIALS SUMMARY REPORT

1.0 INTRODUCTION

1.1 BACKGROUND

In early FY 1980, the Department of Energy (DOE) established the Materials Characterization Center (MCC), managed by Pacific Northwest Laboratory, to provide the materials data base and supporting documentation needed to ensure safe disposal of nuclear wastes. The data base will contain information on components of the waste emplacement package, which includes either the spent fuel or processed waste form, the engineered barriers, and their interaction with the host environment. The MCC will plan materials testing, develop and document procedures, collect and analyze existing materials data, and conduct tests. After test methods and data have been approved by the Materials Review Board (MRB), which is managed by Argonne National Laboratory, the MCC will publish these approved methods and data in a Nuclear Waste Materials Handbook. The first edition of this handbook is to be issued in September 1981.

The MCC has held workshops to obtain the broadest possible consensus that a particular approach to testing will yield suitable and interpretable data. Workshop participants have been experts from universities, industry, DOE laboratories, and government agencies. Previous workshop topics have included leaching, corrosion, and radiation effects.

The Workshop on Compositional and Microstructural Analysis of Nuclear Waste Materials was held in Seattle, Washington, on November 11 and 12, 1980 at the Battelle Seattle Research Center, to discuss the status of current analytical methods and to identify problems in their application. Discussions generally emphasized application to nonradioactive simulated waste materials being studied for waste-package development.

1.2 PURPOSE OF THE WORKSHOP

Most of the MCC test data will result from applications of appropriate analytical procedures to waste-package materials or the products of performance tests. Therefore, it is imperative that the analytical methods in all laboratories be reliable, of known accuracy and precision, and comparable with methods used in other laboratories and on other nuclear waste materials. It was assumed that each laboratory would continue to use those analytical methods, procedures, and techniques for which it is most experienced, proficient, and best equipped.

Therefore, the purpose of this workshop was to

- A) Identify the analytical methods favored by the workshop participants, with suggested applications and expected detection limit, accuracy, and precision;
- B) Discuss "trouble spots" or weak areas that need attention, both industry-wide and locally;
- C) Develop recommendations regarding the optimum means to verify interlaboratory correlation and comparability of analytical data.
- D) Provide a list of specific standards and reference materials currently used in the laboratories represented, including sources and recommendations for use.

1.3 ORGANIZATION OF THE WORKSHOP

The workshop began in a plenary session, with reviews summarizing the role of MCC in the nuclear waste-form process and illustrating the types of analyses required in some of the MCC test procedures under development. The three participants from NBS surveyed the analytical methods in use at NBS and other laboratories. The essential role of careful statistical evaluation of all analytical data was also reviewed.

The major effort of the workshop was conducted in subsequent meetings of three working groups concerned with the following topics:

Group 1. Analysis of Liquids and Solutions

Group 2. Quantitative Analysis of Solids

Group 3. Phase and Microstructure Analysis

Participants in each group are listed in Appendix A. Each group established its own agenda under the direction of the group chairman, using guideline questions sent earlier to members of each group (Appendix D). Approximately equal time was devoted to discussions of 1) identification and evaluation of analytical methodology currently in use, and 2) recommended procedures for assurance of accurate interlaboratory evaluation of analytical data. Each group summarized its initial discussions and recommendations in a draft report.

At a final plenary session, participants discussed major conclusions of each working group, particularly emphasizing the proposed means of interlaboratory correlations.

1.4 ORGANIZATION OF THIS REPORT

This report represents the consensus and experience of the experts at the meeting, concerning several aspects of the analysis of materials that are considered to be most in need of discussion. No attempt is made to formally document information presented by participants, although references are included for some of the data presented. Similarly, the tabulations of analytical methods characteristics, detection limits, relative merits, and similar information are summations of the participants' informal contributions and discussion, and individual citations generally are not given.

Sections 2, 3 and 4 of this report summarize the comments and conclusions of participants of all three working groups regarding standard reference materials, interlaboratory data correlation, and the perceived role of statistical data evaluation of MCC data. Sections 5, 6 and 7 summarize discussions of specific methods, as voiced in both plenary sessions and working group meetings, corresponding to the three working group topics.

The appendices also include a list of participants with addresses and telephone numbers, a summary of the workshop agenda, and an informal list of the working-group discussion topics. Appendix E lists the analytical methods discussed, including some which were simply reported to be in use by participants. The methods are tabulated by laboratory location, including the names of persons reported to be responsible for that work at each laboratory. Also included in that tabulation is a brief list of shielded or contained instruments available for application to radioactive nuclear waste materials.

2.0 INTERLABORATORY DATA CORRELATION

The most vigorously discussed subject of the workshop was the difficult problem of assuring reliable interlaboratory correlation of data. As mentioned repeatedly by workshop participants, the evaluation of performance of MCC waste forms depends heavily on analyses of compositions of a wide variety of materials. Implicit in any comparison of data obtained in different laboratories is the assumption that each laboratory would obtain nearly identical data on tests of identical materials. That assumption is further based on the expectation that the analytical capabilities of each laboratory are of demonstrated competence, and are properly controlled so that the degree to which test data differences represent the tested material or imposed conditions, and not just the methods of analysis, is ascertainable.

However, experiences reported by several workshop participants (ASTM C 26.05 Draft 3 1980; Sill 1980; ASTM Subcommittee D-19.12 1980; Powell et al. 1979) emphasized that the assumption that all laboratories obtain similar data is very likely to be wrong. The primary source of this conclusion was the personal experiences of several participants with analytical round-robin test series. These round-robin tests covered a variety of analytical requirements, both in the U.S. and abroad, in such diverse subjects as trace elements in water, uranium ore analyses, X-ray diffraction (XRD), surface analyses, and radionuclide determinations.

2.1 ANALYTICAL ROUND ROBINS

The consensus of participants regarding the role of round-robin tests in interlaboratory correlations was as follows:

- 1) A round-robin test is an absolutely necessary procedure to establish a firm basis for confidence in subsequent interlaboratory correlations of test results. There is no other effective way to establish that confidence.
- 2) Individual laboratories generally can demonstrate acceptable analytical precision internally, based on data collected routinely in the laboratory. Fewer laboratories regularly use certified reference

standards to check their own accuracy, and only occasionally is an interlaboratory correlation conducted outside the local corporate structure. A round-robin test fills that need.

- 3) Round-robin sample exchanges are a highly effective means for analysts to identify their laboratory's deficiencies. The first sample series in a round-robin test should be for that purpose, rather than simply to demonstrate laboratory conformance. Subsequent rounds of comparison analyses then will demonstrate effectiveness of steps taken toward achievement of interlaboratory agreement.
- 4) Internal checking using reliable known standard materials should be applied routinely in every laboratory for continuous self-monitoring. However, internal checking by each laboratory individually is not a satisfactory substitute for demonstrating ability and interlaboratory agreement on test samples, as in a round-robin test.
- 5) Even seemingly simple routines such as correct identification of spectrum lines, calculations of true concentrations from measured data, and preparation of calibration standards are subject to unrecognized operator error. Round-robin comparisons can frequently point out such errors.

The specimens to be used for a round-robin test pose a special problem, since they must be stable, homogeneous, and available in large enough quantity to provide enough sample from the same source for all participants. Primary emphasis needs to be given initially to solutions analysis and to quantitative solids analysis, since these two areas (especially the former) are key steps in the early MCC round-robin tests.

Considerable discussion in Group 1 led to an offer by Claude Sill of EG&G to devise a recipe for stable solutions suitable for round-robin use. Sill subsequently provided the information for PNL to mix the solutions and distribute to all MCC-1 round-robin participants.^(a)

(a) Samples of the proposed solutions, and wafers of the PNL 76-68 (mod) glass, were prepared and distributed by MCC during November 1980 for the analytical round-robin package sent to all MCC-1 round-robin participants.

Members of Group 2 concluded that a single bar of the PNL 76-68 (mod) simulated waste glass, fabricated in September 1980 by Penberthy Glass, would be an acceptable source for the first solid round-robin specimens for quantitative analysis. Wafers would be cut and distributed from a single bar, with reference pieces from portions adjacent to the distributed wafers to be retained at PNL for analysis in case of questions of source homogeneity. Analyses at PNL by inductively coupled plasma (ICP), X-ray fluorescence (XRF) and microprobe of several similar bars of that material have demonstrated that single-bar homogeneity is within tolerable limits ($\pm$ ~10% relative) for this purpose.

Round robins for surface analysis of solids and for XRD are also important, but are of less immediate need. For surface studies, use of a freshly fractured surface of the same PNL 76-68 (mod) glass proposed for quantitative solids analysis was suggested by Group 2 (surface analysis) participants. To minimize the effect of environmental factors (e.g., humidity) and any other surface preparation variables, specimens must be fractured just before use at each individual laboratory, using a glove bag backfilled with dry nitrogen or argon. The objectives of the initial analyses in this round robin would be to compare spectra obtained for the same elements and concentrations, as well as sensitivity factors for these elements calculated from the known average bulk concentration. This information would be the essential first step in correlating quantitative surface analyses of vitreous nuclear waste forms. However, a surface analysis round robin was not considered a high priority requirement now.

Group 3 participants concluded that a quantitative phase determination round robin would not be worthwhile now. The XRD quantitative methods are insufficiently developed for meaningful comparison, and no suitable standard specimens could be proposed. Instead, development of a microprobe standard was considered more important. For near-term use, the PNL 76-68 (mod) glass was suggested for microprobe comparison; it appears to be largely single phase, and thus can be used for cross-check or calibration against other solid bulk analysis procedures.

2.2 ALTERNATIVES TO ROUND-ROBIN METHODS

Two alternatives to the round-robin method of interlaboratory correlation were discussed briefly and concluded to be less satisfactory. The first was individual use of in-house or purchased standards, supplied periodically to the analytical laboratories as blind or routine specimens by users of the laboratory services rather than originating with the laboratory supervision. This procedure was concluded to be essential in establishing and maintaining analytical capability within any laboratory, but it is not the equivalent of comparing skills with other laboratories. In the view of several participants, all laboratory personnel naturally tend to interpret their data toward the known values. The conclusion was that while, in theory, the internal checking should be satisfactory, in actual practice it proves inadequate for establishing proof of laboratory performance. A large part of that inadequacy may be simply the general view of "outsiders," who generally tend to mistrust self-measurement procedures.

The other alternative discussed was the establishment of laboratory "accreditation" procedures similar to those conducted by the National Voluntary Laboratory Accreditation Program under the direction of the U.S. Department of Commerce and the NBS (Unger 1980). Accreditation practice would follow the guidelines established in ASTM Standard E 548 by ASTM Committee E-36 (Berman 1980; ANSI/ASTM E548-79 1979). For the nuclear waste program, in addition to analyzing standard specimens provided by a designated central reference laboratory, all accredited laboratories could submit both their test data and a few specified samples to a central "reference" laboratory, where verification of the analytical results would be conducted by duplicate analyses in the reference laboratory. However, this procedure imposes a very significant additional work load on the reference laboratory (which therefore requires funding for the task) for both the task of administering the accreditation procedure and for providing the continuing analytical test monitoring. Workshop participants concluded that periodic round robins are much less cumbersome to conduct, and are more directed to the objectives of the MCC.

2.3 CONTINUING DATA QUALITY ASSURANCE

Workshop participants pointed out that achievement of agreement through round robin, accreditation, or other "one-time" procedures is not assurance that data submitted subsequently for routine specimens will always be correct. A requirement for reporting laboratories to always include data obtained by analysis of specified standards, in conjunction with test specimen data, was suggested. No details of such a requirement were attempted.

3.0 STANDARD MATERIALS

Workshop participants concluded that the availability and effective use of standard reference materials, including both solids and solutions, is a critical factor in achievement and maintenance of analytical accuracy, but there is presently little standardization in methods of application or selection of reference materials. Standard reference materials are required for two separate but related purposes: for calibration of instruments and methods, and for periodic independent checks to verify satisfactory routine analytical performance. Reference materials for either purpose must be stable over long periods of time, available in sufficient quantity for frequent repeated use, be of the same composition range and physical form (e.g., solutions, bulk pieces, or powders) as the specimens to be analyzed, and have a documented record of homogeneity.

Participants agreed that none of the available certified reference standard materials is completely suitable for nuclear waste studies, and that an urgent need exists for one or more such standards.

3.1 CALIBRATION STANDARDS

The first application of standard materials is the initial calibration and periodic recalibration of each analytical instrument to provide the reference points on which all subsequent analyses are based. These standards must contain a known concentration (with uncertainty estimated) of the elements to be determined, and must contain no other interfering components. These standards need not be completely similar in overall composition to the samples to be analyzed, but careful allowance must be made for possible matrix effects, or behavior differences between relatively pure standards and the complex specimen mixtures on which the analysis will be used. Generally, a graded series of three or more concentration levels is needed for calibration purposes.

Calibration standards for known elemental concentrations in solutions are most often prepared from pure metals, or by direct use of individual solutions or mixtures of solutions obtained from speciality supply houses. Special precautions must be observed in mixing standard solutions, especially those

offered commercially. A standard value for concentration of a specified element does not assure the absence of all other (possibly interfering) elements, and reactions such as precipitation may occur between ions or incompatible compounds present in the initial individual standard solutions.

In addition, special attention must be given to storage of solutions (Moody 1977; Subramanian et al. 1978). Most participants use polypropylene or polyethylene bottles for storage of solutions containing ≤ 1 g/liter concentrations for maximum periods of 1 to 4 months before discarding. The analytical atomic absorption group at NBS stores more concentrated solutions (5 to 10 g/liter) in Pyrex[®] volumetric flasks always used for the same element; exceptions are Si, B, and HF-containing solutions, which are stored in polypropylene.

For solid materials analysis, the most common standards are single stoichiometric compounds. Mixtures can be prepared by blending powdered materials thoroughly and pelletizing for analysis if desired. Such powdered mixtures are most applicable for analytical methods such as XRF and XRD in which normal sample preparation includes grinding to a specified mesh size. Solid microprobe standards are commercially available in metallographic mounts from several sources as pure metals, stoichiometric compounds, or as homogeneous minerals supplied as independently analyzed secondary standards.

Participants agreed that all materials used for methods calibration need specific evaluation for each application, especially for the possible presence of interfering or unlisted components. This precaution applies particularly to mixed solutions used for spectrometric methods; trace quantities of contaminants may easily exceed detection limits for sensitive elements. Frequency and method of application of standards as calibration checks differ widely among the laboratories. Table 1 illustrates typical practice for solutions analysis; a generally similar range of practices was discussed for solid materials analytical methods.

Table 2 contains a tabulation of standard calibration materials currently in use by the participants' laboratories. None of these materials appears to be traceable to the NBS.

[®]Pyrex is the trademark of Corning Glass Works, Corning, NY.

TABLE 1. Frequency of Application of Calibration Standards for Solutions Analysis by Participating Laboratories

Laboratory	Method	Frequency and Comment
Argonne National Laboratory	AA and ICP	<ul style="list-style-type: none"> - batches of samples are bracketed with three standards - controls are run at intervals - blanks are run to check for memory effects
	Colorimetry	<ul style="list-style-type: none"> - calibration curve is prepared for each set of samples from standards
Catholic University	DCP	<ul style="list-style-type: none"> - high and low standards before and after each sample series - recalibration applied to each block of specimens
Exxon Nuclear	AA and ICP	<ul style="list-style-type: none"> - run sample followed by bracketing standards; therefore 2 standards per sample are run - one of every five samples receives a spike
NBS	AA and DCP	<ul style="list-style-type: none"> - same as PNL - also use method of standard additions (spike) at a concentration of 50% - 150% of analyte to check for matrix effect, recovery, etc.
Oak Ridge National Laboratory	AA and ICP	<ul style="list-style-type: none"> - a standard is run after every 3-4 samples, or minimum of once each day - a control is run daily for each analysis - long-term observation of the control data serves as a check on the stability of the method - when the analyzed value for the standard differs from the known value by >2 RSD, the method is recalibrated - method of standard additions (100% - 150% of analyte) to check for matrix effect, recovery, etc.
PNL	ICP	<ul style="list-style-type: none"> - standard run after every 3-4 samples - recalibrate when $\pm 3\%$ ($\pm 5\%$ for alkalis) relative deviation or drift is noted; linear correction to samples run since last calibration or standard
	AA	<ul style="list-style-type: none"> - one standard per sample
Rockwell-Hanford	ICP	<ul style="list-style-type: none"> - calibrate single elements at 5 different levels in a multielement matrix - calibrate every 4 hours - check blank for solution memory effect and drift - if there is drift, recalibrate with 1 standard and blank

TABLE 2. Standard Materials Currently Used by Workshop Participants for Analytical Methods Calibration

<u>Material</u>	<u>Source</u>	<u>Application</u>
Aqueous solutions (single element and multielement)	Alpha Ventron; Fisher; Spex Industries	Atomic emission and absorption spectrometry standards
Solid oxide powder; pure metals; single crystals; other pure compounds	Spex Industries Johnson-Mathey; AD McKay	Preparation of spectrometry solution standards; pelletizing for XRF and XRD; microprobe; SEM/EDX
Mounted and polished metals and compounds	Charles M. Taylor Co.; J.C. Rucklidge	Microprobe; SEM/EDX
Silicon powder	U.S. National Bureau of Standards (NBS-SRM 640)	XRD

3.2 REFERENCE STANDARDS

Reliable reference standards, representative of the specimens being analyzed routinely, need to be included in the specimen stream as "blind" samples regularly to demonstrate controlled analytical accuracy and precision. Careful attention to standards data assures consistency of analytical data on unknowns and early detection of uncontrolled problems. These standards must be as similar as possible to the overall composition of typical specimens to minimize differences in matrix or interelement effects. To verify method accuracy the standard must also have known concentration values, preferably certified by a recognized source such as the NBS. When only relative accuracy and precision need to be known (as when comparing sequential runs or different instruments or procedures), nominal concentration values are sufficient, but specimen homogeneity and stability are essential.

There are no totally suitable certified analytical reference standards available for nuclear waste materials; that is, none of the available certified standards contains a composition representative of the nuclear waste specimens, either as solid or solution. The NBS is currently preparing both solids and solutions for these purposes; but development, testing and certification is

expected to require about two years of work. Two alternatives are available to participants in the meantime. One is use of the several NBS-certified standards of glass, cement, and mixed component powders that are available (NBS 1979). Each by itself is insufficient or only partially applicable to MCC requirements, and is useful for method verification only within those compositional limits. However, use of several of those standards can provide a highly useful appraisal of analytical procedures. Compilations of analyzed values for these and other reference materials by several U.S. and foreign laboratories have been published (Gladney 1980; Abbey 1980).

The other alternative is utilization of a reference glass such as the PNL 76-68 glass. This material is in no way certified regarding composition or homogeneity, but is an approximation of "typical" waste composition. A "secondary standard" working reference material of this type can be utilized to detect analytical method differences, such as interelement effects affecting one procedure but not another, and to monitor precision and relative accuracy between analyses, methods, or instruments (within homogeneity limits of the material). While material of this type is certainly no substitute for a certified standard, it can provide many of the functions of a standard on "best-available" interim basis for the complex nuclear waste mixtures.

Table 3 contains a tabulation of NBS-certified standards presently in use by participating laboratories.

3.3 REAGENT PURITY

Several workshop participants emphasized the importance of the use of "standardized" high-purity reagents in preparing both elemental solutions standards and test solutions such as reference leachants. Despite the significant role of the residual impurities contained in the water and acids used, insufficient attention often is paid to obtaining and maintaining reagent quality commensurate with the very low element concentrations of interest in leaching tests. Suitable equipment and methods are readily available for reagent purification (Kuehner et al. 1972).

TABLE 3. NBS-Certified Standards Currently Used As Analytical References by One or More Workshop Participants

Materials	Standard Reference Material Identification	Description
Water solution	1643a	Trace elements (ng/g)
Glass powder	89 91 92	Lead-barium Opal Low boron
Glass (plate and wafers)	93a 620,621 610-617	Borosilicate Soda-lime 61 trace elements, ~5 ppb to 500 ppm
Refractory (powder)	76a, 77a, 78a 103a 198-199	Burnt refractory ($Al_2O_3-SiO_2$) Chrome Silica
Cement	633-639	Portland
Organic matrix	1571-1577	46 elements, 0.1 ppm to 5%
Fly ash	1633a	22 trace elements
Si (powder)	640	XRD internal standard
Oxides (powder)	674	5 oxides for quantitative XRD intensity reference

Table 4 compares typical residual impurity content of water purified by three different methods. The potential effect on analytical specimen detection limits is self-evident; analytical blank analyses need to be included as a regular part of each laboratory's standards program (Murphy 1976).

TABLE 4. Residual Impurity Observed in Purified Water

Purification Method	Concentration, ppb	
	Si	Na
Triple distillation	15	20
Ion exchanger	5-20 ^(a)	5-20 ^(a)
Redistilled in Teflon®	0.5-2	1-2

(a) Drift upward during use of each ion exchanger cartridge.

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4.0 THE ROLE OF STATISTICS IN NUCLEAR WASTE ANALYSIS FOR MCC

The characterization of nuclear waste forms and the prediction of their long-term behavior under diverse environmental conditions is a data-dominated project. That is, the comparative suitability of the various proposed waste forms is to be determined primarily from data obtained from many performance tests conducted under a wide range of conditions. Most of the test data are from quantitative analyses conducted during the test procedures. Since final conclusions can be no better than the quality of the test data, accurate evaluation of the reliability of those data is absolutely essential.

Since many different laboratories utilizing diverse methods and staff are producing the data, a means of verifying data compatibility from all sources must be provided. The best means is the combination of analysis of reference materials for interlaboratory comparisons (round robins) and application of sound statistical methods to determine the significance of any observed differences in analytical results.

4.1 CURRENT PRACTICE

Workshop discussions revealed that while all participants agreed that statistical evaluation of analytical data is useful, no common practice is being followed (Sill 1979). The current use of statistical methods by workshop participants range from casual or occasional calculations of precision all the way to maintaining complete on-line computer files of all laboratory data and frequent systematic determination of precision and relative accuracy from those data. The latter procedure provides a nearly ideal record, which permits early identification of "out-of-control" methods, contaminated working solutions, comparative skills of personnel and overall quality of laboratory output. Unfortunately, it also requires a significant investment of time and special equipment, beyond the capabilities of most supporting analytical laboratories.

Nevertheless, workshop participants acknowledged that without accurate statements of "confidence limits" and other evidence of data quality, direct comparison between laboratories is uncertain at best. As a minimum, workshop

participants agreed that every data set reported should include a statement of the estimated precision for each element or analysis, a brief explanation of the basis for those estimates, and, if possible, the analysis of a standard or reference material of similar type to demonstrate the relative accuracy expected.

4.2 DEFINITIONS

Part of the problem in estimating precision and accuracy of data is in defining the terms. A discussion of the terms is included in the ASTM Annual Book of Standards (ANSI/ASTM E 177-71 1979). Absolute accuracy is very difficult to determine; the most common approach is by comparison with a "known" reference standard, from which the probable bias of the analyses can be estimated. However, standard materials of accurately known composition are generally lacking for complex nuclear waste mixtures. So, instead, relative accuracy is more often measured, obtained by a comparison of analytical results obtained in several laboratories, preferably by several different methods. Thus, biases or errors built-in to a particular method or laboratory can be recognized by their large divergence from the mean of the remaining data, even though the true value is not known specifically.

Precision is commonly expressed in terms of the calculated standard deviation. However, the procedure for obtaining the data from which the precision is calculated needs to be clearly specified. Methods described by workshop participants included the following:

- a) precision of successive repeated analyses on aliquots of a single prepared sample (which gives short-term, instrument-related information only)
- b) same as a), but at various extended time intervals (which combines longer term instrument performance information, and specimen stability data)
- c) complete analysis of duplicate specimens from the "as-received" condition through to final data (to factor in all steps involved in the analysis that could contribute to errors, e.g., by operator, instrument, reagents, environments, etc.)

For precision to be truly representative of the actual analytical method, all individual data points need to be completely independent and uncorrelated, and need to include all steps in the procedure such as sampling, sample preparation, and instrument operation. With proper experiment design, the magnitude of errors associated with each stage of the procedure can be estimated separately.

Rarely is completely uncorrelated data possible, but analysts should aim in that direction. Otherwise, the precision reported may be very significantly overestimated, possibly leading to misinterpretation of apparent differences between analyses of different materials or between laboratories.

Detection Limit also has various definitions, usually based on the observed analytical signal relative to the precision determined at higher concentration. For example, one simple definition of detection limit is "that concentration in a dilution series where the measured value equals twice its standard deviation". Similarly, for methods utilizing pulse counting techniques, the detection limit can be defined as equal to twice the background count. Another definition is "the minimum concentration which is detected above background (not necessarily estimated precisely) a fixed proportion of the time, e.g., 50% or 95%." Whatever method is used, analytical reports should define the term and list the value for each element. Regardless of the listed limits, however, analytical data reports should always report the concentration actually measured (not simply "less than detection limit") to allow statistical comparison of data obtained from other laboratories using different detection-limit definitions.

4.3 RECOMMENDED APPLICATIONS

An important reason for carefully defining the statistical basis for the analytical data reported was emphasized repeatedly in discussions at the workshop. When complex tests or sample preparation procedures precede the actual analysis, the repeatability of final test results depends on the combination of both the test procedure and the analytical method. But both the test procedure and the subsequent analysis contribute individually to the total

bias measured in the final result. Therefore, the contribution of each step to the total precision must be known in order to properly understand the final experimental results.

Finally, participants repeatedly emphasized that precision, accuracy, and detection limits are matrix-dependent, and are sensitive to the effects of changing sampling conditions, concentration levels, combinations of elements, and particular analytical procedure. Statistical evaluations need to be conducted for each combination of conditions; it should not be assumed that the same evaluation pertains to any but the singular set of conditions for which the data were obtained.

5.0 ANALYSIS OF LIQUIDS AND SOLUTIONS

Members of Working Group 1 were as follows:

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Mabil Morcos, Brookhaven National Laboratory
Aaron Barkatt, Catholic University
Claude Sill, EG&G
Ted Lyon, Exxon Nuclear Idaho Co.
Chuck Bazan, Lawrence Livermore Laboratory
Jim Merrill, MCC
Mike Epstein, National Bureau of Standards
Dan Costanzo, Oak Ridge National Laboratory
Frank Hara, Pacific Northwest Laboratory
Barry Scheetz, Pennsylvania State University
Clarence Homi, Rockwell Hanford Operations
Charles Coleman, Savannah River Laboratory
Miles Myers, Atomic Energy of Canada

Participants in Working Group 1 discussed analytical methods that can cope with the diversity of requirements imposed by nuclear waste solutions and the related performance tests. Element concentrations may differ over a very wide range, from major components of dissolved solid samples to trace quantities of elements leached from an "inert" solid surface. Both conditions may co-exist in the same solution; that is, trace contaminants may be of concern in a dissolved solid specimen or in a high-solids-concentration solution such as brine. In addition, the number of elements in any one sample may range from one or two to more than 30. Properties of interest may include, in addition to concentrations of dissolved elemental species, the pH of the solution and the form and concentration of anions present. Further problems occur in preserving the integrity of solutions, especially in very low concentrations and in materials difficult to dissolve.

5.1 ANALYTICAL METHODS

Workshop discussions centered around the methods currently in widest usage for solutions. The methods are listed in Table 5.

5.1.1 Activation Analysis

Neutron activation analysis (NAA) is a powerful multielement analytical tool, applicable to as-received specimens in either liquid or solid form. The primary limitation is the need for a suitable neutron activation source. A detailed discussion of activation analysis is included in the next section, "Analysis of Solid Materials". Discussion of the application of NAA techniques to the measurement of leaching of simulated solid waste forms has been published (Flynn et al. 1979).

5.1.2 Atomic Spectrometry

Atomic spectrometry is the most widely used method of solutions analysis, largely because of the multielement capability and speed of the plasma techniques, the low detection limits for both emission and absorption methods, and wide availability of suitable instruments (Dean and Rains 1975; Kingston et al. 1978; Feldman and Rains 1964; Fassel 1978; Floyd et al. 1980). Currently available techniques may be summarized as follows.

5.1.2.1 Emission Methods

In emission spectrometry the specimen solution is injected into a high-temperature excitation source. The excitation of the elements present produces the characteristic elemental lines, which are then isolated by the spectrometer to reach appropriately located photomultiplier detectors. The intensity of the lines from the atomic vapor produced in this high-temperature cell is a measure of the elemental concentration. A major reduction in matrix effects results from the much higher temperature (6000°–8000°C) achieved in ICP excitation using an argon atmosphere, compared to a simple flame or arc source. The ICP is the most free of interferences of any of the atomic spectrometric techniques that are available. However, there are some spectral interferences, that is, interferences of the analyte lines with lines of other elements that occur in the plasma.

TABLE 5. Primary Methods Used by Participants for Elemental Analysis of Solutions

Method	Typical Techniques	Applications	Working Range	Limitations
Activation Analysis	Neutron source exposure + peak height analysis	Multi-element; low trace elements	(a)	Neutron source required
Atomic Spectrometry	ICP	Simultaneous multi-element analysis	1 ppb to 1000 ppm	Spectral interferences
	DCP	Simultaneous multi-element analysis	1 ppb to 100 ppm	Spectral interferences
	Flame atomic emission	Simultaneous multi-element analysis	<100 ppb to 100 ppm	Chemical and spectral interferences
	Flame atomic absorption	Sequential elemental analysis	10 ppb to 10 ppm	Chemical interferences
	Electrothermal atomic absorption	Sequential elemental Analysis	0.1 ppb to 0.1 ppm	Chemical and molecular absorption interferences; transient (~1 sec) signal
Electroanalytical Methods	Ion chromatography	Anion analysis	10 ppb to 100 ppm	
	Polarography	Anion analysis	10 ⁻⁵ to 0.01 M	Substances capable of cathodic reduction or anodic oxidation

(a) Variable depending on analytical equipment and specimen; typically ppb to pure element.

The simultaneous multielement capability of atomic-emission sources is based on the emission of all elemental radiation from a single location in the source. This allows the source radiation to be focused on a grating spectrometer, which has an individual exit slit positioned on the focal plane at the wavelength of each of the elemental lines to be monitored. While these simultaneous "direct-reader" systems provide a significant increase in analytical speed and reduction in sample volume, the choice of elements to be analyzed is essentially fixed by the initial choice of exit slit positions. Sequential systems, which employ a single exit slit and scan from one element wavelength to the next, are much more flexible, but require significantly more time and sample volume. Instruments combining fixed and sequential modes are now available commercially.

Direct current plasma (DCP) methods have recently been improved to the point where they are competitive with ICP in some respects. The DCP, instead of being produced by an alternating field, is produced by a direct current in argon between two carbon anodes and a tungsten cathode. DCP is slightly more susceptible to interelement interferences than ICP and the use of consumable electrodes limits continuous operating time to 3 to 4 h. However, there are techniques, such as using lithium buffers, that will reduce interferences to the point where the DCP is about equivalent to an ICP. The major advantage of the DCP (due to the commercial instrument that is available) is the use of an echelle high-resolution spectrometer. Consequently, a trade-off must be made in selecting ICP or DCP; ICP has a better tolerance to interferences, while the improved spectral resolution of the echelle spectrometer of the DCP provides an improved spectral interference tolerance. The echelle grating appears to be more susceptible to stray light interferences, however.

ICP still remains the preferred analytical method for solutions. It has been widely investigated and utilized in many diverse applications in recent years; new problems encountered generally relate to the specific materials analyzed. While the ICP has been combined with an echelle spectrometer, problems dealing with the source viewing area still have to be resolved.

5.1.2.2 Absorption Methods

Absorption spectrometry requires a stable radiation source (e.g., hollow cathode lamp) that provides radiation corresponding to the electronic transition for each element of specific interest. The sample is atomized in a high-temperature absorption cell by a flame or electrothermal means. Ten to 100 times better sensitivity results from electrothermal atomization of a sample confined in a graphite tube compared to the open flame. The increased sensitivity is attributed to a longer residence time of atomic vapor in the absorption cell. Quantitative measurements are made of the amount of attenuation of the standard source radiation on passing through the sample atomic vapor in the absorption cell. Analyses usually are conducted sequentially using a radiation source for each element of interest. However, a technique recently developed and undergoing in-service testing at the U.S. Department of Agriculture in Beltsville, Maryland uses a xenon-arc continuum source, which provides a continuous and intense spectral distribution over the range of 190 to 800 nm. The radiation, after passing through the absorption cell, is isolated by an echelle spectrometer and detected by an array of photomultipliers placed appropriately as for a DCP spectrometer. The system can determine up to 20 elements simultaneously in a flame or graphite furnace by atomic absorption (AA). Since it employs a wavelength spectrometry technique, some additional advantages of this system over normal AA systems are 1) it does not suffer from the usual limited linear range of AA (it has approximately the linear range of emission spectrometry, e.g., ICP), and 2) it provides an automatic background correction for molecular absorption.

The single-element procedure usually associated with absorption spectrometry limits its use in nuclear waste application to problems not amenable to ICP or similar approaches. Cesium analysis is a prominent example. While emission techniques generally provide lower detection limits for the alkali elements than does absorption, the argon spectrum interferes with the sensitive cesium line in plasma excitation. Using AA with a graphite furnace instead, a detection limit of 0.005 ppm can be achieved. With a brine matrix (high concentrations of sodium, potassium, and magnesium chlorides), a graphite furnace

cannot be used, but flame source atomic absorption is still much more sensitive (~0.5 ppm) than ICP on the diluted brine.

Another element often best analyzed by AA is ruthenium. The complexity of behavior of Ru during analytical procedures is caused by the ability of Ru to exist in several different oxidation states, each with a different vapor pressure of compounds in solution, and each plating out on container surfaces or precipitating at a different rate. Therefore, if the prior history of the Ru-containing sample is not known, or the absence of the highly-volatile Ru⁺⁸ cannot be verified, appropriate preparation steps are recommended to assure reduction to Ru⁺⁶. Effective methods include fusion of solid samples in KOH-KNO₃, and distillation of Ru-containing solutions from a perchloric acid solution into dilute HCl-hydroxylamine. The resulting Ru⁺⁶ oxidation state does not have a volatile oxide, and therefore can be analyzed by ICP. For low concentrations of Ru, the graphite furnace AA method is used; hydroxylamine hydrochloride must be added to liquid samples containing nitric acids. The nitric acid apparently tends to oxidize the Ru during the drying and charring cycle of the analysis, resulting in formation of ruthenium tetroxide. The addition of hydroxylamine hydrochloride reduces the Ru to a lower oxidation state, preventing the volatilization of Ru as tetroxide.

5.1.2.3 Comparison of Spectrometric Methods

Relative advantages of spectrometric methods, especially as applied to nuclear waste solutions, are summarized in Table 6. (See also Table 5.)

Simultaneous multielement capability is essential for analysis of many elements in a small amount of sample. The best methods for that purpose are the ICP, DCP, and the continuum source AA (multielement) system.

High precision is always important. It is especially so when analyzing solutions such as brine in which a very high contamination blank occurs. Such blanks cannot be overcome simply with good detection limits. Instead, the higher the precision of the technique, the closer the actual differences between blank and true solution concentrations can be measured. For that

TABLE 6. Comparison of Spectrometric Methods

	Best		Worst	
Multielement capability	ICP, DCP, CSA		FAA, ETA	
Inherent precision ^(a)	FAA	ICP, DCP	ETA	
Chemical interferences	ICP	DCP	FAA	ETA
Spectral interferences	FAA	DCP	ICP	ETA
Detection limits	ETA	ICP, DCP	FAA	

ICP = inductively coupled plasma

DCP = direct-current plasma

FAA = flame atomic absorption

CSA = continuum source atomic absorption (flame and electrothermal)

ETA = electrothermal atomic absorption

(a) The precision obtained under optimum conditions where variation in the analyte signal, and not the background, is the limiting source of noise.

purpose, flame AA has the best precision (~0.3%). The ICP and DCP generally give precisions of ~1%; with electrothermal AA, precisions are ~2% to 3% with an automatic sampler and ~5% with manual sampling techniques.

Minimizing chemical and spectral interferences is also essential, although complete elimination cannot always be achieved. To avoid interelement interferences, the higher temperature utilized by ICP makes it the best method. The DCP is slightly inferior to ICP, then flame AA, followed by electrothermal AA. For spectral interferences, flame AA is least affected. The DCP is superior to the ICP, mainly due to the detection system with the echelle spectrometer. (Presumably, an echelle spectrometer applied to an ICP also would result in fewer interferences.) Electrothermal atomization is poorest because of the problems with scatter and molecular absorption.

Finally, for low limits of detection, electrothermal AA is by far the best method in the absence of interferences. ICP and DCP are approximately equivalent, and flame AA has the poorest sensitivity.

Table 7 compares typical detection limits obtained in noninterfering matrices using several spectrometric, colorimetric, and activation analysis methods. Individual laboratory practice and instruments will determine limits actually attainable.

5.1.3 pH Measurements

Although the determination of pH is nominally a simple, straightforward use of standardized equipment and procedures, several interfering factors may prevent reproducible results. Careful control of measurement conditions is especially important when the significance of observed pH values in leach experiments is still uncertain, and the relationship of pH to leach mechanisms is not yet understood.

When determining the pH of the MCC standard brine, the pH probe must be calibrated in a solution of equal ionic strength. Thus, the standard commercial buffers must be adjusted with respect to ionic strength, for example by the addition of KCl or dilution with a concentrated solution of KCl.

TABLE 7. Typical Detection Limits for Solutions Analysis by Spectrometry and Colorimetry (see also Table 6)

<u>Element</u>	<u>Typical Detection Limit, ppb</u>			<u>Colorimetry</u>
	<u>ICP</u>	<u>DCP</u>	<u>FAA</u>	
B	10	5	50,000	50
Ce	40	50	--	--
Cs	--	--	15	--
Fe	5	2	100	0.3
Na	10	2	2	--
P	100	100	5,000	0.5
Si	20	10	400	0.5
Sr	2	2	--	--

The determination of pH in weakly buffered solutions is not straightforward and requires careful attention. Data show that even very small sorption of CO_2 into the solution dramatically affects the pH. Relatively stable pH readings can be obtained within three minutes by excluding atmospheric CO_2 during the pH determination. The method used to measure the pH must be selected carefully. For example, glass electrodes generally are more reliable than pH paper, since the indicators used in the paper provide more buffering capacity than the solutions themselves.

5.1.4 Anion Analysis

Anion analysis is of concern primarily in connection with solutions involved in waste-form leach tests. Although the concentrations of major waste elements and the principal components of the matrix are the first concern in short-term leach tests, anion analysis is important in identifying anionic species in the leachant that may react with nuclear waste solids. Such data significantly assist in understanding leach mechanisms. Anionic species originating both in the leachant and in the waste form have important effects on the long-term pH, and on the ensuing rate of corrosion. Suitable methods are available to characterize the anionic composition of the leaching medium, particularly groundwater, and to determine the levels of anionic species leached out of the waste form.

Of the commonly used anion analysis methods, ion chromatography systems have performed most satisfactorily. Significant improvements have been made recently, such as the use of dual-column systems for the simultaneous operation and regeneration of columns. A Dionex[®] ion chromatography system has been used successfully for the determination of F^- , Cl^- , Br^- , NO_3^- , and SO_4^{2-} . The development of bipolar pulsed conductivity detectors, which eliminate the need for a suppressor column, has been reported. These detectors can also be applied to the analysis of monovalent and divalent cations. Silicate and borate species, though negatively charged, are usually determined as Si and B by techniques such as emission spectroscopy. Detection limits by ion chromatography are about 0.5 mg/liter and can be further improved using preconcentration techniques.

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Anions that pose special problems include NO_2^- and SO_3^{2-} , which are susceptible to oxidation on the column, and CO_3^{2-} , which can be measured only at high concentrations and under ideal conditions. Elimination of the high level of predominant anions from the eluent can improve the detection limits with respect to trace anions. In certain cases, specific ion electrodes can provide more sensitive detection, e.g., for total carbonate (detection limit of ~1 mg/liter) and F^- (0.02 mg/liter). Lower levels of carbonate species can be determined by means of infrared analytical methods, which are, however, more complicated, expensive, and of limited applicability.

5.2 SPECIFIC PROBLEMS IN SOLUTIONS ANALYSIS

The reliability of solution analysis is highly dependent on ensuring that a truly representative sample is analyzed under conditions optimized for the particular analytical method applied. Various pretreatments of the as-received sample may be required, e.g., to stabilize and preserve the original sample, recover trace elements plated on the vessel walls, allow for any particulate matter present, concentrate the dissolved constituents to improve analytical accuracy, or modify the solution to optimize analytical condition.

5.2.1 Pretreatment

Additional sample pretreatment or additions to the leachate samples may be required, depending on the particular analytical method employed. Examples include use of lithium as a buffer solution for the DCP, alkali metals as ionization suppressants for flame AA spectroscopy, or matrix-modification agents for graphite furnace AA (Sill 1961).

5.2.2 Preconcentration

Preconcentration of solutions may be a necessary or convenient means of obtaining improved analytical information, particularly after short-term leaching tests or with nearly inert test materials in which elemental concentrations are below the detection limits. Separation and concentration of trace elements contained in brine solutions may be required for adequate sensitivity (Kingston 1978).

A promising method which is under development at Lawrence Livermore Laboratories for the concentration of leachates from the flowing leach experiments involves the preconcentration of the leachate by evaporation at 60 C in Pyrex beakers, followed by evaporation to dryness in Teflon beakers in the presence of Avicel® (a microcrystalline cellulose). The dry material is then pressed into a thin wafer and analyzed as a solid by XRF or neutron activation methods. Initial data indicated some possible problems with quantitative recovery of the analyte. Concentration factors of 100 to 1000 may be achieved, leading to detection limits of 50 ppb starting from 100 ml of solution. The procedure is applicable to U, Th, Ca, Mo, As, Pb, and other elements.

Specific methods for recovery of individual elements of interest can also be used if their importance justifies the additional time and effort required. For example, two methods are available for leachate concentration of Cs in leachates. Good accuracy and precision can be achieved by precipitation with ammonium molybdophosphate, separation, dissolution in NaOH, extraction into sodium tetraphenylboron/cyclohexane-hexone, and determination by flame emission AA. Detection limits for Cs are about 0.005 µg/ml of solution burned. In another method currently under development for concentrating Cs, sodium tetraphenylboron is added directly to 100 ml of the aqueous solution. About 100 µg of Ru carrier is added. The precipitate is collected on Millipore® filter, and the amount of Cs present is determined as a solid by XRF. Potassium interferes with these methods; hence, the methods would be unsuitable for the determination of Cs in solutions such as brine containing large concentrations of K.

5.2.3 Preservation of Solutions

To assure preservation of solutions such as ground waters for cation analysis, HNO₃ is generally used (preferably high-purity; e.g., Ultrex®), added at a concentration of about 1% to 2% (0.2 to 0.4 M). Nitric acid is preferred instead of HCl because the latter may cause chemical interferences in some analytical techniques, particularly for Cs analyses using the graphite

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furnace AA method. Brines containing Cl must be acidified with HCl, however, to avoid the deleterious effects on equipment of chloride-nitric acid mixtures.

5.2.4 Plateout

Loss of leachate elements by plating out on the walls of containment vessels during the leaching process is a significant problem at very low concentrations. The suggested recovery procedure is treatment of the leaching vessel with 1 M HNO_3 for at least 12 h at 90°C or higher. This treatment may be inadequate for some elements. Instead, a mixture of 8 M HNO_3 and 1 M HF can be used to ensure that most elements are redissolved. However, this latter method would result in losses of Si and B and would also increase analysis time, since the HF would have to be removed before analysis by ICP where silicate glass equipment normally is used. Alternatively, the DCP or ICP could be used with the Teflon-coated sample introduction tubes that are available for those instruments.

5.2.5 Particulates

Solid particles suspended in solution to be analyzed may occur under several conditions. Total dissolution of complex waste ceramics or glasses is often difficult; solution of solid components may be incomplete, or the initial solution may be unstable so that precipitates occur on standing. Similarly, during leach tests the solution of a soluble phase in the waste form may release insoluble phases, resulting in a two-component leaching product. Therefore, the analyst must be constantly alert to the possible occurrence of solids in solutions to be analyzed.

Solid particles left suspended in solutions may lead to incorrect analyses, because of the inability of the analytical procedure used to handle particles and solutions simultaneously. Vaporization and excitation of spectra (absorption or emission) for the solids is likely to differ from the process with solutions. In addition, equipment such as fine-tip nebulizers may not function reliably when particles are included in the liquid stream. Some analytical techniques, such as graphite furnace AA, may be less subject to particle-size effects and may thus give better analytical results than techniques that employ solution nebulization. Nevertheless, the particulate

problem must be considered on a case-by-case basis since the accuracy of analytical results may depend on its resolution. Ultrafiltration and separate analyses of the solution and particles collected is obviously an alternative method.

6.0 ANALYSIS OF SOLID MATERIALS

Members of Working Group 2 were as follows:

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John Russ, North Carolina State University

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Tom Thomas, Pacific Northwest Laboratory

Alan Harker, Rockwell-International

Dave Johnson, Savannah River Laboratory

David Clark, University of Florida

Discussions by workshop participants emphasized repeatedly that several different analytical methods are required for the diverse problems in the study of solid materials. The objectives of analyses of solid samples range from obtaining an average composition for the entire bulk specimen to quantitative analyses of selected features or of surface layers. Good analytical methods are available and in use for each type of application, and the appropriate methods must be carefully selected. For example, the choice of analytical method is strongly influenced by the structure of the material to be analyzed; microprobe methods give useful information regarding the entire specimen of a homogeneous single-phase glass, but apply only to the specific site examined on a polycrystalline multicomponent ceramic. Similarly, different procedures may be selected for analysis of a heterogeneous material, depending on whether general screening information or detailed understanding of the microstructure of individual components of the system is required. The true meaning of the term "homogeneous" as applied to analyzed material depends as much on the method used to determine homogeneity (and thus the microlevel to which it applies) as on the specimen itself.

The methods most commonly used for nuclear waste solids analysis are summarized in Table 8. During the workshop all these methods were reviewed and

TABLE 8. Primary Methods Used by Workshop Participants for Analysis of Simulated Nuclear Waste Solids

Method	Typical Practice	Applications	Limitations
X-ray Fluorescence	X-ray tube excitation	Qualitative or quantitative analysis of powdered or solid specimens	Surface penetration of ~1 mm; significant matrix effects; requires standards for quantitative data
Electron Microprobe	Electron beam excitation	Solid specimens; usually concurrent with electron microscopy	Surface penetration of ~1 μm ; limited area of analysis; quantitative method requires specific standards; matrix effects
Atomic Spectrometry	Dissolved specimen analysis by ICP, DCP, or AA methods	Multielement quantitative analyses of bulk specimens	Entire specimen must be dissolved
Neutron Activation	Activated spectrum analysis of liquid and solid samples	Multielement analysis of complex mixtures, including very low concentrations	Requires activation source; quantitative analysis requires simultaneous analysis of standards
Near-Surface Emission Spectroscopy	Spectral analysis from low-energy excitation by electrons, ions, or X-rays	Analysis of thin surface layers, reaction zones	Surface penetration of 2 to 200 $\text{\AA}$; expensive specialized instrumentation required; quantitative data not commonly acquired; data interpretation requires experience

compared for applicability, advantages, and limitations. Although the more common applications of each method are listed in Table 8, this list is by no means exhaustive, and all methods have been utilized by the participating laboratories in a variety of situations. Such practices are generally considered acceptable, provided that the conditions of use are carefully recorded, and appropriate known reference materials are analyzed in the same manner concurrently to verify that acceptable data are produced.

6.1 X-RAY FLUORESCENCE

The most commonly used bulk analytical method currently appears to be XRF using X-ray tube excitation. Wave-length dispersive sequential methods provide maximum peak separation and allow detection limits of at least 0.1%; some users report limits of 10 ppm and below for most elements. Energy-dispersive systems provide a multielement spectrum from each excitation period, thus reducing analysis time, but requiring use of curve-stripping techniques to interpret the spectra of complex mixtures (Shann and Russ 1977).

The bulk of the time required for XRF analyses is in sample preparation. For assurance of representative data (e.g., in multicomponent glass), the sample may be finely ground, diluted if needed to reduce the matrix effect, and fused with sodium tetraborate or other binder to prepare a solid pellet for analysis. Alternatively, the powdered sample may be mounted directly for analysis. The estimated time for analysis is 20 to 40 min/sample. Small grain specimen material (e.g., multiphase SYNROC with grain sizes of 1 to 3 μm) can be analyzed as-received, since X-ray path lengths equal several particle diameters.

Matrix effects can be handled by any of three methods. The most common, dilution to reach the linear range of calibration curves, reduces concentration of trace elements, but makes standardization easy. For undiluted materials, comparison standards of a composition similar to the specimens are needed, but for complex mixtures none is generally available. A "fundamental parameters" method can be used instead with suitable instrument software. This method consists of obtaining the necessary interelement correction coefficients by analysis of a few specimens of known composition, even if very different from

the unknowns. Data precision of $\pm 5\%$ relative can be obtained by this technique, except at trace levels where counting statistics limit the precision. Similar methods using proton excitation (especially for thin-film analysis) were reported also.

6.2 ELECTRON MICROPROBE

XRF spectra are also produced by high-energy electron-beam excitation and can be recorded for analytical purposes concurrently with electron microscopy or in a dedicated electron-beam instrument. Specimens may be any solid form, but a polished specimen surface is strongly recommended for quantitative data. If the particular information provided by a fracture surface is of interest (e.g., inter- or intra-granular composition), special methods are needed (generally based on excitation at two different accelerating voltages) to correct for the differing surface tilt angles (Russ and Hare 1980). In addition, existing "ZAF" equations are needed to convert X-ray peak height data to concentrations, correcting for interelement and matrix effects. The depth of penetration of the electron beam must be considered in evaluating the significance of analyses. Beam energies of at least 15 kV generally are needed to excite elements of interest, resulting in a roughly spherical analyzed volume about $1\mu\text{m}$ deep; because of the relatively small volume analyzed, detection limits are generally about 0.05% to 0.1%. For the same reason, considerable care needs to be exercised in extrapolating microprobe data to total sample composition. Also, the possibility of localized modification of the surface by the electron beam must be recognized. Possible effects include dehydration in the vicinity of the beam spot, and Na migration induced by surface charging or thermal diffusion from beam heating.

Electron-beam excitation can be utilized for analysis and correlation of components in multiphase specimens, e.g., in single grains of hollandite (Russ et al. 1980). Methods integrating data from several grains also have used backscattered electron imaging to identify grains of interest from their apparent composition, measuring peak/background ratios to obtain analytical

information. In a fracture analysis, the microstructure itself is an important factor; e.g., inter- and intra-granular fracture modes provide different kinds of compositional information relative to the total specimen.

Various modes of microprobe information display are available, including selected or sequential point analysis, line profiles, and X-ray maps for specific elements.

Additional discussion of microbeam methods for phase analysis is reported in Section 7.2.

6.3 ATOMIC SPECTROSCOPY

Atomic emission and absorption spectroscopy have long been used for multi-element analysis of solids. However, the severe matrix effects often encountered with DC-arc or spark-source excitation of the solid sample result in significant limitations in many applications, particularly when quantitative information is needed. The relatively recent development of high-energy plasma excitation, e.g., ICP and DCP, has renewed interest in atomic spectroscopy because of the greatly reduced interference or matrix effect in the plasma. For solid materials a new problem has resulted, however, that of totally dissolving the solid specimen for injection into the plasma stream.

Most of the relatively inert materials comprising nuclear-waste-disposal systems can be dissolved by severe acid treatment such as with HF or HF-HCL in a reaction bomb. However, under these conditions, glass components cannot be used in the analytical instrument and other methods are required for silicates (Sill 1961). As an alternative, the sample can be fused with Li_2CO_3 , $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{KOH}-\text{KNO}_3$, Na_2O_2 , or KF . Borate fusions must be avoided in ICP instruments in which boron is to be analyzed because of the high sensitivity of the instrument to residual boron on internal surfaces. Some ceramic materials, such as mullite, can be dissolved in HNO_3 -HF, fumed to near dryness, and redissolved in 5 M NH_4OH . There is no appreciable HF reaction of the solution with ICP glass components.

Fusion does not guarantee total solubility of the specimen, and special care must be used to ensure that all components are in fact dissolved and remain in solution. For example, most fused glass samples will dissolve in dilute HCl. However, some oxide or calcine samples, especially those containing significant amounts of rare earths, will not completely dissolve using KOH-KNO₃ fusion; complete dissolution is generally obtained with a Na₂O₂ fusion. Samples containing Zr and high concentrations of phosphates will not dissolve when acidified with HCl. The addition of oxalic acid will dissolve the zirconium phosphate, but the rare-earth oxalates will slowly precipitate from solution. The ICP analysis on these samples must be performed as soon as possible after sample dissolution. Since KF fusion is followed by H₂SO₄, Na₂SO₄, then HCl to dissolve the fused sample, the presence of Ba, Sr, and high levels of Ca causes sulfate precipitates. Such precipitates tend to quantitatively carry actinide and lanthanide species and have to be filtered and redissolved separately. Precipitation is common after a period of time for many samples dissolved by fusion. The precipitate should be identified and treated according to its own chemistry. For example, titanium will precipitate in the presence of sulfates or K; H₂O₂ may be used to redissolve the complexes formed.

Some limited use of plasma methods for analysis of small particles as suspended solids, rather than totally dissolved material, has been reported. Particles estimated to be smaller than 10 μm are said to carry satisfactorily into the atomic vapor for ICP or DCP excitation.

It can be concluded that application of atomic spectroscopy methods by dissolution of solids is most satisfactory for simple mixtures. However, the uncertainties of achieving and maintaining total solution for complex multicomponent inert solids suggest that a reliable solid-state analytical procedure is to be preferred where available.

6.4 NEUTRON ACTIVATION

Activation analysis is a nuclear method of elemental analysis that determines elements regardless of their chemical or physical state and is therefore

particularly applicable to as-received specimens, both liquid and solid (Guinn 1971). The method gives no information about the chemical forms or valence states of the elements detected. It can be a very fast method; in many cases, samples can be completely analyzed in a matter of minutes. Also, if sufficiently high fluxes of neutrons are used, the method is extremely sensitive for a large number of elements. In fact, the method is the most sensitive one known at present for the quantitative determination of the majority of the elements of the periodic system. The dynamic range of the method is large, extending rigorously from the limit of detection up to the pure element itself.

Because of the high penetrability of neutrons and gamma rays in most matrices, the range of practical sample sizes is very large, extending from microscopic samples up to many grams. Since the absolute limits of detection of the various elements worsen only moderately with increasing sample size throughout this size range, the method is especially powerful for the detection of low concentrations. Thus, for a typical element, detectable down to 0.001 μg , the concentration limit of detection is 1000 ppm in a 1- μg sample and 0.001 ppm in a 1 g sample. Matrix effects generally are not encountered except in the presence of high thermal-neutron cross-section elements such as B. The presence of certain elements (e.,g., Na, Cl) may cause very high background counts, and the short-lived induced activity must be allowed to decay before measurements can be made.

The major disadvantage of activation methods for many laboratories is the need for an activation source. While thermal neutrons from a reactor are most commonly used, charged particles, high-energy protons or electrons from a suitable accelerator, or a high-energy gamma source can all be used instead. Analytical cost is high (\$100 to \$200 per element) for purchased analytical service, but if an activation source is available, the method can be competitive in cost and accuracy with ICP methods. For quantitative analyses, a comparator method with simultaneous irradiation of known (standard) materials is commonly used. Agreement with other analytical methods appears to differ in various laboratories, from good to as poor as a factor of two or three difference. The method applies particularly well to detection of differences ("ratioing") and to the detection of very low concentrations, where no other analytical methods are conveniently usable.

In leach-test procedures, activation methods can be used to monitor the course of leaching by analyzing both the original bulk solid specimen and the resulting leachate. Since the activation step need be applied only to the solid sample before leaching tests are applied, very low elemental concentrations of leached activated species can be detected in the leachant without interference from the containment vessel (Flynn et al. 1979).

6.5 SURFACE SPECTROSCOPY

As proposed nuclear waste forms are shown to be relatively unreactive, the role of surface reactions in total long-term waste-package stability becomes more important. Well-established methods such as electron microprobe and XRF are useful for such studies, but as materials become more nearly inert the reactive surface layer becomes considerably thinner than the μm - or mm-penetration depth of those techniques. Therefore, methods for monitoring near-surface ($<200 \text{ \AA}$ deep) phenomena, particularly the changes occurring under simulated waste storage conditions, assume great importance.

Because of the increasing potential value of surface techniques, and the special experience and interest of several workshop participants, a subgroup of Working Group 2 discussed this technique in greater detail. Members of the Surface Analysis Group were M.T. Thomas (Chairman), N.S. McIntyre, A. Harker and D. Clark.

6.5.1 Comparison of Surface Methods

A family of analytical methods suitable for this work has been developed in the past few years, based on the detection, identification, and semiquantitative evaluation of various emissions resulting from irradiation of the surface of specimens with appropriate particle probes (Table 9). Techniques currently being used include Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Rutherford backscattering spectroscopy (RBS), and nuclear microprobe spectroscopy (NMS). The spatial resolution and depth analyzed can vary widely, as summarized in Table 9, depending on which of these probes is used, and what equipment is available.

TABLE 9. Characteristics of Surface Analysis Spectroscopy Techniques

Method	Probe Use	Depth Analyzed	Resolution	Detection Limits, ppm	Primary Use
X-ray Fluorescence	X-ray beam	1-2 mm	10-20 mm	1	Average composition
Electron Microprobe	High-energy electrons	0.5-1 μm	0.5-1 μm	50 (500, low Z)	Microfeatures analysis
Auger Electron	Low-energy electrons	2-30 $\text{\AA}$	500-5000 μm	1000	Low Z elements; micro-analysis of phases
X-ray Photo Electron	X-ray beam	2-30 $\text{\AA}$	4 mm	1000	Chemical state information
Secondary Ion Mass	Ion beam	2-30 $\text{\AA}$	1 mm	0.01-100	Trace element analysis; H determination; rapid sputter profiling
Rutherford Back-scattering	High-energy alpha particles	200 $\text{\AA}$	2 mm	100-100,000	Quantitative analysis; depth profiling without sputter sectioning; hydrogen analysis
Nuclear Microprobe	High-energy ions (D, p, O, F, others)	200 $\text{\AA}$	2 mm	100-100,000	Same as for RBS

6.5.2 Typical Applications

Several important applications of near-surface probe methods apply to nuclear waste evaluation, in addition to helping develop atomistic models of such phenomena as waste-form leaching and canister corrosion. For example, in waste-form leaching tests, the following measurements by near-surface probes can help ensure that standard tests on materials are reproducible:

1. Analyze the specimen surface before leach testing to verify that it is representative of the bulk; that it is not contaminated with impurities that can change the leach rate; and that specimen preparation in different laboratories produces surfaces of the same initial composition.
2. Analyze the specimen and leaching container surfaces after leaching tests, to verify that any elements that precipitated out of solution have been retrieved from the container walls, and that no interaction has occurred between specimen and container. These tests need not be performed on every specimen, but on selected ones after sample-preparation procedures have been developed.

6.5.3 Problems in Applying Surface Methods

Because the phenomena being measured are surface related, any prior history of exposure to excessive moisture or other reactive environment, e.g., careless contacts with fingers or containment vessels, will produce anomalous surface composition data. In general, specimens for surface analyses should be held in a spring-type mount to avoid possible introduction of contaminants from epoxies or conducting paints.

Other potential sources of problems are specimen charging, sputtering, misinterpretation of data and inadequate standards. Specimen charging is particularly troublesome with AES and SIMS. By employing low-energy (<5 eV) ion and electron sources, much of the charging can be minimized or avoided. In addition, optimum adjustment of current density, incident energy, and angle of incidence can help in minimizing charging. However, some specimens cannot be analyzed with AES or SIMS without neutralizing beams. A higher energy (>500 eV) electron neutralizing beam is particularly useful for SIMS analysis of insulating glasses.

All of the techniques except RBS and NMS require ion-beam sputtering to obtain elemental depth profiles by sequentially removing thin surface layers and analyzing the newly exposed area. Sputtering is a complex phenomena that must be used with caution. It is important to calibrate the sputtering ion source parameters and to measure the sputtering rate on the samples being profiled. A good standard material that can be used for that purpose is SiO_2 , particularly when working with glasses. Knowing the sputter rate allows the conversion of sputter time to a known depth. If the rate changes, as it does in leached reaction layers, the depth scale becomes nonlinear. When doing ion-sputter depth profiles, signals from the edge of the sputter crater can be misleading. One way of avoiding this problem with XPS, which samples a large surface area, is to have specimens about 5 mm^2 and sputter over the whole area. When doing SIMS, the common techniques to avoid edge effects is electronic raster gating; that is, SIMS data are acquired only when the ion beam is in the center of the crater.

6.5.4 Calibration Techniques

Since considerably less development of these methods as a routine analytical tool has occurred than for traditional analytical methods, and because of the inherent difficulties in interpreting surface-related information, the procedures are most often used as qualitative or semiquantitative procedures. XPS, AES and SIMS can be made quantitative by the use of standards, but only a few really suitable surface standards are available.

Since published sensitivity factors for AES or XPS are often not applicable to complex matrices, a useful practice is to obtain a bulk specimen analysis from independent measurements to normalize the data and provide empirical sensitivity factors for that matrix. Standard NBS specimens, e.g., stainless steels or glasses, can be used by ductile-fracturing them in the electron or ion spectrometer. Surface analyses by AES of the fresh fracture surface can then be indexed to the bulk elemental concentrations.

A similar method can be used with SIMS. For example, NBS 610 glass and GSC SY-3 geologic standards have been used to determine sensitivity factors

for SIMS, referencing all elements to Si. The sensitivity factors for these two glasses are fairly similar for B, Al, and other low-Z elements. Trace-element profiles have been obtained on leach glasses using SIMS sensitivity factors obtained in this way. The sensitivity factor for B seems to be independent of the matrix and is a good monitor of reactions in a glass reaction layer.

Matrix effects are important in determining the sensitivity factors; the factor for the same element may differ significantly depending on the system under study. Also the probing beam (whether electron, ion, or X-ray) can cause matrix effects. For example, it is often necessary to cool insulating specimens that contain Na or other alkali metals to minimize the alkali ion mobility.

7.0 PHASE AND MICROSTRUCTURE ANALYSIS

Members of Working Group 3 were as follows:

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Working Group 3 addressed the applications of analytical methods required for identification and measurement of specific phases and the correlation with microstructure. It was recognized that the distinction between solid materials elemental analysis and phase and microstructure techniques is not sharply defined. For example, XRF microprobe analysis, discussed also by Group 2, is clearly applicable to determination of elemental composition of individual phases, while XRD and infrared reflection spectroscopy (IRRS) are volume-averaging techniques for determination of certain specific phases.

Several additional problems are encountered upon going from average elemental analysis of materials to specific phase and microstructure analyses. The most obvious problem is that of the rapidly increasing complexity of the system as the number of individual components increases, particularly in crystalline materials. The number of possible combinations of constituents present is the result of prior sample history, the nature of starting components, and sample preparation procedures; the phases actually observed are also dependent on the resolution of the observation instrument.

A complete structural understanding of a material requires a combination of at least three complementary analytical techniques. Microscopy--optical,

scanning electron, or transmission electron--reveals the existence of a multiphase system, and the spatial interrelationship of visually observable components. Quantitative analysis of the microscopy images can be conducted to estimate the volume fraction of each component, but their identity (composition) usually cannot be determined by microscopy alone except by implication from known materials of similar appearance. Microbeam techniques can reveal the elemental composition of individual phases, and can be applied simultaneously with microscopy when using electron imaging methods, either as SEM/EDX combination instruments or as TEM/STEM instruments applying analytical electron microscopy. However, XRD measurements are necessary to determine the specific combinations of those elements comprising the crystalline compounds present. Alternatively, infrared spectroscopy or scanning calorimetry methods can be utilized to help identify amorphous or glassy phases.

A summary of the characteristics of these analytical methods is given in Table 10.

7.1 X-RAY DIFFRACTION

Phase analysis by XRD has been an established tool of analytical chemistry for more than four decades, and remains the only universally applicable method of determining how elements are combined in crystalline phases. However, the quality of the data obtained is heavily dependent on the skill, technique, and experience of the X-ray specialist. Important factors include specimen preparation, size of particles and phases present, availability of appropriate standards, and complexity and concentration of phases present.

7.1.1 Specimen Preparation

The importance of controlled techniques in specimen preparation for XRD cannot be overemphasized. Best reproducibility is achieved with samples prepared as powders ground to <325 mesh. Care must be taken to ensure that all the sample passes through the screen; otherwise the grinding merely separates the friable phases from the more resistant ones. However, it is not always possible to unambiguously identify components of multiphase systems, especially those with structures of low symmetry. If at all possible, analyses of single crystals separated from the initial sample should be conducted.

TABLE 10. Primary Methods Used by Workshop Participants for Analysis of Phases and Microstructure

Method	Typical Techniques	Applications	Limitations
Microscopy	Optical, SEM, TEM	Identify phases by micro-structure; quantitative phase measurements by image analysis methods.	Qualitative identification by metallographic methods
Microbeam Analyses	Electron probe, alone or with SEM or TEM	Individual phase elemental analyses; electron diffraction	Low-Z elements may not be detected; minimum analytical diameter, ~1 μm with SEM, <100 $\text{\AA}$ to 1000 $\text{\AA}$ with TEM; TEM sample preparation difficult
X-ray Diffraction	Spectrum analysis of powders or single crystals	Phase analyses in complex mixtures	Applicable only to crystalline phases; some minor phases may not be detected; quantitative methods uncertain
Infrared Spectroscopy	Reflection methods	Detect phase changes in glass	Semiquantitative; phases not identified
Scanning Calorimetry	Temp. v. expansion coefficient	Monitor crystallization of glass matrix	Empirical calibrations; phases not identified

When analysis of bulk specimens is required, particular care must be taken during sample preparation to ensure that secondary phases (e.g., those developed during leaching) are not destroyed. This generally precludes sample polishing since leaching is primarily a surface reaction.

7.1.2 Phase Identification

Powder XRD should be used for all samples. The diffractometer should be well aligned; Guinier or Gandolfe methods may be used. All data should be reported, including d-spacings and intensities. It is preferable to include a photomicrograph of the sample with the X-ray data. For samples that are nearly all glass, and consequently have few lines, the radial distribution can be reported.

In indexing an unknown XRD pattern of a mixture, every peak must be accounted for, including the small ones. Often a SEM/EDX elemental analysis of the same or similar crystals is needed to specifically identify a phase. Thus, the SEM/EDX is used to observe the individual phases present and obtain an elemental composition, and XRD of the powdered specimen then is applied to identify the specific crystalline compounds corresponding to the elements previously identified. Often SEM/EDX maps then can be prepared for each phase by selecting elements unique to each phase. In addition, SEM/EDX will identify those species having a crystal size too small for sharp XRD peaks, generally about 1 to 2 μm or smaller.

7.1.3 Quantitative Measurements of Crystallinity and Phase Changes

While XRD is most widely used for determining composition of crystalline phases, the intensity of peaks corresponding to specifically identified phases is related to the percent of crystalline phases within the specimen. However, reliable routine procedures for making quantitative measurements have not been developed. The existing procedures compare the X-ray pattern of specimens with those of mixtures of a noncrystalline matrix to which known proportions of a standard crystalline material have been added. The method assumes that the peaks characteristic of the specimen develop in the same way as those of the "generic" crystalline standard (e.g., Al_2O_3) in the prepared mixture. Not only is the assumption unlikely to be true in the case of complex systems such

as nuclear waste mixtures, but additional factors such as grain size and grain orientation introduce significant perturbing factors. Quantitative analysis (determination of the relative amounts of each phase present) can be achieved reliably only in simple totally controlled systems, because of the matrix effect on spectra as compositions change, and the subtle spectral differences that occur with addition of even small amounts of chemically similar species to an otherwise known system. Depending on the type of waste-form samples, it may be possible for individual investigators to prepare mechanical mixtures of specific phases to establish calibration curves. In any case, differences between otherwise similar specimens can at least be estimated for useful semi-quantitative comparisons, by observations of relative peak heights, without having made an absolute calibration. For these reasons, semiquantitative XRD analyses are usually reported as estimated composition ranges rather than firm values.

An alternative method to determine the amount of each phase present is based on a procedure referred to as "normative calculations" in petrology. It requires that the bulk composition of the sample be known with precision, all phases be crystalline with no solid solution, the composition of all different phases in the sample be known by XRD identification, all phases be larger than 10 μm , and grain-to-grain homogeneity be demonstrated. From these data, calculations can be made of the necessary distribution of components of the bulk to form the so-called "normative phases" identified by XRD. Calculation of fraction of each phase present follows. In practice, this method can benefit greatly by the application of electron microprobe methods to obtain quantitative analyses of all elements present. A good homogeneous microprobe standard for nuclear waste glass is needed for this purpose; the glass standard under development at NBS is expected to fill this need.

7.1.4 Recommended Procedures Summary and Limitations

The sample must be ground so that all of it passes through a 325-mesh sieve. Scan rates should not be faster than $1/4^\circ$ θ per minute. All spectrum lines must be identified and intensities compared with NBS Al_2O_3 , α -quartz (SiO_2), or CeO_2 intensity standards. Intensities should be measured by peak area, either graphically or by step scanning over peaks.

While most laboratories have access to X-ray diffractometers samples available only in small quantities may require use of camera techniques. Consequently, alternate X-ray methods should include Guinier, Gandolfi, and micro-diffractometer techniques. Whether for quantitative phase determination or simply phase identification, it is imperative to describe the analytical methods and standards used and the basis for selection of the standard in each analytical report.

Phase composition information can be obtained from crystals in the 3 to 4 μm size range, but good chemical data on a routine basis require phases in the 10 to 20 μm size range. The limit of detection of crystal phases in glass is about 3 wt%, while in multiphase crystalline material the limit may be as high as 5 wt%, depending on crystal size and quality. There are computer methods available to enhance spectra by stripping away background, which in some systems may improve precision and lower detection limits.

7.2 MICROBEAM METHODS OF PHASE ANALYSIS

As stated previously, the identification of phases by XRD is easier if elemental information is available. Electron-beam methods are recommended for that purpose. The SEM/EDX method has been discussed in the previous section relative to analysis of solid materials and can be applied to individual phases $>1\ \mu\text{m}$ in diameter. For phases smaller than 1 μm , analytical TEM or STEM using microbeam techniques is the only available method. TEM/STEM use is limited because the sample area that can be examined is small, and the required sample preparation methods are difficult and time consuming; however, it can be used to study and identify phases as small as 30 $\text{\AA}$ diameter, by XRD and electron diffraction methods. Selected area electron diffraction information is often a valuable adjunct to XRD when mixtures of complex phases are encountered.

The quality of supporting electron microprobe (EDX) analysis also depends on grain size and the amount of element present. The influence of concentration on the standard deviation of data for microprobe analysis of a SYNROC sample is illustrated on Table 11.

TABLE 11. Examples of the Precision of Microprobe Data as a Function of Concentration

	<u>Reported</u> <u>Concn.,</u>	<u>Relative</u> <u>Std. Dev.</u>	<u>Reported</u> <u>Concn.,</u>	<u>Relative</u> <u>Std. Dev.</u>	<u>Reported</u> <u>Concn.,</u>	<u>Relative</u> <u>Std. Dev.</u>
Sr	0.2 $\pm$ 60%		0.8 $\pm$ 12%		2.4 $\pm$ 2.3%	
Cs	0.2 $\pm$ 60%		0.9 $\pm$ 25%		4.2 $\pm$ 2.5%	
U			0.3 $\pm$ 50%		11.0 $\pm$ 2.0%	
Ce	0.15 $\pm$ 75%		0.9 $\pm$ 6%		2.6 $\pm$ 3.0%	
Nd	0.2 $\pm$ 60%		0.6 $\pm$ 20%		1.8 $\pm$ 9%	

7.3 QUANTITATIVE MICROSCOPY

Quantitative microscopy methods are essentially extensions of the classical optical microscopy point-counting methods (Underwood 1967). Of themselves they provide a partial understanding of microstructure--estimates of the quantities of various phases observed, without identifying the phases. Combined with analytical methods such as XRD and microprobe for phase identification, additional information may result. Since the information is obtained primarily by instrumental measurements and summation of microstructural features, the quality of data is highly dependent on the quality of the microscopy techniques used. Measurement methods (even automated instrumental procedures) may be time consuming, but often provide quantitative information not obtainable any other way.

Quantitative estimates of the following values can be obtained by quantitative microscopy and image analysis:

- magnitude of dimensions of distributed phases
- degree of dispersion of distributed phases
- volume fraction of distributed phases
- amount of interfacial area/unit volume
- average volume of grains, cells, or distributed particles
- distribution of particle sizes
- three-dimensional information by serial sectioning

The results obtained depend on how well individual phases can be identified, on the number of fields chosen for counting, and on how representative

the fields are of the total volume of the material. The greater the surface area of the section of sample, the better the accuracy will be. Even if XRD is used for quantitative phase determination, representative photomicrographs (either optical or SEM) are useful in physical interpretation of the numerical and chemical data.

7.4 INFRARED REFLECTION SPECTROSCOPY

When information regarding relative durabilities or changes in species or structural content of a material is needed (rather than compositional information), IRRS is useful. The equipment needed is relatively straightforward and requires no special skills to operate for reliable data. Specimen preparation is equally simple, utilizing samples from 1 cm² up to several centimeters with a flat surface polished to 600 grit. The beam is about 0.5 cm square. Information is obtained to a depth of about 0.5 μ m, so that data represent an average condition and are not affected by small heterogeneities. The resulting spectrum is sensitive to surface alterations due to corrosion and leaching. It can be used to monitor the state of the specimen (e.g., glasses versus crystalline), and thus provides some structural as well as limited compositional information. The infrared method is particularly useful in comparing large numbers of samples, e.g., for rapid screening; it is relatively rapid (15 min/sample) and inexpensive (a few dollars/sample). Since the infrared method does not provide compositional information directly, it must be used in conjunction with other specific methods (e.g., XRD) to identify components present. However, when species have been identified and a particular spectrum thus calibrated, changes can easily be monitored semiquantitatively.

The method is sensitive to changes in specimen composition of 1% to 5% of the constituent, using a conventional instrument, and to a few ppm change if a Fourier-transform infrared (FTIR) instrument is available to provide much more sensitive spectrum interpretation. Data reproducibility is about $\pm 2.5\%$ relative (better with FTIR).

A typical application of IRRS is the comparison of corrosion modes occurring during leach tests of a series of glasses, illustrated in Table 12.

Although relatively few laboratories are using infrared methods, the advantages would suggest that it should be seriously considered for sample screening and similar uses. The cost ranges from about \$15,000 for a conventional instrument to \$40,000 or more for FTIR equipment.

Table 12. Types of Glass Corrosion Modes Distinguishable by Infrared Reflection Spectroscopy

<u>Corrosion Type</u>	<u>Description</u>
I	Inert, no change
II	Stable SiO ₂ film
III	Protective film formation
IV	Unstable film formation
V	Congruent dissolution

7.5 SCANNING CALORIMETRY

The degree (amount) of crystallinity present in an amorphous matrix such as glass can be measured by scanning calorimetry. The maximum value observed in the plot of expansion coefficient versus temperature can be calibrated as a function of total crystallinity. As with other methods, quantitative reliability depends on calibration against a similar (identical components) material. Under good operating conditions, crystal fractions down to 3% to 5% can be determined with a relative accuracy of about 3%.

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APPENDIX A

WORKING GROUP MEMBERS

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WORKSHOP AGENDA

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J. L. DANIEL, TECHNICAL CHAIRMAN

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WORKSHOP AGENDA

BATTELLE SEATTLE RESEARCH CENTER

J. L. DANIEL, TECHNICAL CHAIRMAN

<u>Monday, November 10</u>	8:00 pm	Informal Social Hour Apartment C-5
<u>Tuesday, November 11</u>	7:45 am	Coffee - Seminar Lobby
	8:15	Outline of Workshop Activities Role of MCC in Waste Management Role of Analytical Data in Waste-Package Characterization Analytical Methods Review: <ul style="list-style-type: none">- Analysis of Liquids and Solutions- Quantitative Analysis of Solids- Phase and Microstructure Analysis Role of Statistics in Evaluation of Analytical Data Problems and Procedures for Analysis of Hot Waste Forms
	10:40	Break
	11:00	Organization of Working Groups
	11:15	Working Group Sessions (Establishment of Individual Working Group Agenda)
	12:15 pm	Lunch
	1:00	Working Group Sessions
	3:00-3:30	Group Chairmen Schedule: 15 min. break
	5:00	Cocktail hour - Apartment C-5
	6:00	Dinner - BSRC Dining Room
	7:30	Group Leaders prepare first draft of summary reports
<u>Wednesday, November 12</u>	7:45 am	Coffee - Seminar Lobby
	8:15	Full Workshop Meeting: Brief group progress reports

8:45	Working Group Sessions: Completion of summary reports
11:00	Break
11:15 am	Full Workshop Meeting: Group summary reports <ul style="list-style-type: none"> - Liquids and Solutions Analysis Recommendations
12:15 pm	Lunch
1:00	Full Workshop Meeting: Group summary reports <ul style="list-style-type: none"> - Solids Analysis Recommendations - Phase Analysis and Microstructure Recommendations - Standard Reference Materials; Sources and Application
3:00	Break
3:15	General Discussion
4:30	Adjourn

APPENDIX D

WORKING GROUPS' DISCUSSION TOPICS

APPENDIX D

WORKING GROUPS' DISCUSSION TOPICS

WORKING GROUP 1: LIQUIDS AND SOLUTIONS

1. Analytical Techniques

What are the best tools: UCP, AA, activation, VIS/UV, or other wet-chemical methods?

What are the shortcomings and advantages?

What is the best compromise, subject to suitable control?

2. Dissolution Techniques

How can a totally stable solution be achieved with unreactive waste forms?

3. Concentration Techniques

What quantitative techniques are available?

Which is best when dealing with brine (e.g., 250 g/l dissolved solids, principally Na, K, Mg and Cl) and wanting to concentrate Cs, Sr, Fe, Nd, etc?

4. Separation Techniques

What quantitative methods are available to separate trace elements from solutions, e.g., brine?

What methods are both quantitative and easy to use (specimen throughput is important).

5. Anion Analyses

What methods are available for geochemically important anions F^- , Cl^- , HCO_3^- , CO_3^{2-} , S^{2-} , SO_4^{2-} , etc?

What can be done with a limited amount of solution?

6. Speciation Techniques

In some studies, speciation may be important. For example, a measure of the redox conditions is the ratio of Fe^{++}/Fe^{+++} or As (III)/As (V).

Are quantitative and easy-to-use methods available?

Which is best?

7. Accuracy and Precision

What is necessary and what is sufficient?

What procedures are required to demonstrate and communicate accuracy and precision at the necessary and sufficient levels?

WORKING GROUP 2: SOLIDS

1. Analytical Methods Selection

What are the advantages and limitations of X-ray fluorescence, atomic emission spectra, activation, surface methods, other?

2. Specimen Preparation Methods

How does specimen preparation affect specimen homogeneity, time and cost of analysis, detection limits, and elemental interferences?

What are the relative merits of solid versus powder samples?

3. Surface Versus Bulk Methods

How can surface-science methods, which generally are not quantitative, be used effectively?

4. Quantitative Data Reduction

What methods are available for the qualitative-to-quantitative step in X-ray fluorescence and other methods?

5. Data Reliability

What sensitivity, precision, and accuracy are attainable?

What is "practical" for routine application?

6. Standard Reference Materials

What standard materials are available or under development?

Can any of these standards be utilized for both solution and solid analytical methods?

WORKING GROUP 3: PHASES AND MICROSTRUCTURE

1. Characterization Objectives

What methods are recommended for determination of waste-form microstructure, phase identification, chemical composition of individual phases, structural state of phases (i.e., degree of crystalline polymorphic state), and quantitative amounts of phase present?

2. Specimen Preparation

What procedure is necessary for different waste forms (e.g., glass, glass-ceramics, crystalline, matrix materials, and coated pellets)? How can phase concentration be achieved (e.g. physical concentration, gravity, flotation, centrifuge, partial solution, etc.)?

3. Metallography, Petrography, and Ceramography

What special considerations are necessary for high-quality results?

4. Accuracy Requirements

What is needed for elemental analyses of phases for mass balance considerations, solid solution and stoichiometry determinations, and assessment of waste-form fabrication processes?

5. Data Handling Problems

What specific problems are introduced by spectral interferences, particle-size effects, deconvolution, matrix corrections, mass absorption corrections, and specific data-reduction methods?

6. Throughput Time and Cost

What are the effects of the above subjects on the cost of analyses?

7. Primary and Secondary Standards

What standards are available, and how can they best be utilized?

APPENDIX E

PRINCIPAL ANALYTICAL METHODS IN USE ON NUCLEAR WASTE MATERIALS
AT PARTICIPANTS' LABORATORIES

Method	Location						
	Argonne	Brookhaven	Catholic Univ.	EG&G	Exxon Nuclear	Lawrence Livermore	Nat. Bureau Standards
1. Metallography & Microscopy	J. Battles R. Arrons						
2. Emission Spectroscopy (ICP, DCP)	E. Huff	M. Morcos	P. Macedo	C. Sill		C. Bazan	M. Epstein
3. Absorption Spectroscopy (AA)	K. Jensen		P. Macedo				M. Epstein
4. Surface Spectroscopy (Auger, XPS, SIMS, others)	C. Johnson V. J. Sethi	S. McIntyre		L. Caspar			G. Hembrey
5. Mass Spectroscopy	L. Callis						
6. Infrared Spectroscopy	G. Reedy						
7. Activation (Neutron, other)	L. Jardine R. Heinrich						G. Lutz
8. X-ray Diffraction	B. Tani			D. Miley		G. Smith	C. Hubbard, S. Block
9. X-ray Fluorescence	E. Kucera						
10. Electron Microprobe	C. Johnson					R. Ryerson, A. Chodos	D. Newberry
11. SEM/EDX	K. Kucera, R. Malewicki J. Bates			D. Miley		R. Ryerson	L. Cook, T. Negas
12. TEM	V. J. Sethi			L. Casper			
13. STEM	V. J. Sethi					C. Echer	N. Tighe, B. Hockey
14. Nuclear Mag. Resonance	V. Maroni J. Rathi						
15. Radiochemistry	L. Jardine R. Heinrich			C. Sill			
16. Radiation Shielded or Contained Instruments	SEM (J. Saneki)						

Method	Location						
	N. Carolina State Univ.	Oak Ridge	PNL	Penn State	Rockwell-Hanford	Rockwell- International	Sandia
1. Metallography & Microscopy			R. Beauchamp		R. Palmer, G. Wolf		
2. Emission Spectroscopy (ICP, DCP)		D. R. Heine	F. Hara	S. Atkinson	C. Homi		
3. Absorption Spectroscopy (AA)			F. Hara	S. Atkinson			
4. Surface Spectroscopy (Auger, XPS, SIMS, others)			M. T. Thomas	G. G. Pantano I. S. T. Tsong			
5. Mass Spectroscopy		J. A. Carter					
6. Infrared Spectroscopy				W. B. White			
7. Activation (Neutron, other)		J. R. Stokely		W. B. Jesty			
8. X-ray Diffraction			H. Kissinger, J. Shade W. J. Weber	B. Scheetz W. B. White	A. Gallagher, R. Johnston		
9. X-ray Fluorescence	J. Russ	J. H. Stewart	R. Sanders J. L. Daniel	B. E. Scheetz P. W. Strickler			
10. Electron Microprobe							
11. SEM/EDX	J. Russ		J. L. Daniel	B. E. Scheetz	R. Palmer, G. Wolf		
12. TEM			R. Jones R. Bradley W. J. Weber				
13. STEM			R. Jones J. Brimhall	B. E. Scheetz	G. Arden		
14. Nuclear Mag. Resonance							
15. Radiochemistry		J. R. Stokely					
16. Radiation Shielded or Contained Instruments		XRD (S. Dismuke) SEM (R. S. Crouse) Probe (R. S. Crouse) Mass. Spec (J. A. Carter) Ion Chromatog. (J. M. Keller)	XRD (H. Kissinger) ICP (F. Hara) SEM/EDX (J. L. Daniel) Probe (J. L. Daniel)		ICP (C. Homi)		

Method	Location			
	Savannah River	UC/Davis	Univ. of Florida	Whiteshell/ Canada
1. Metallography & Microscopy	D. E. Rawl			
2. Emission Spectroscopy (ICP, DCP)	C. Coleman			
3. Absorption Spectroscopy (AA)				
4. Surface Spectroscopy (Auger, XPS, SIMS, others)	P. G. Whitkop			
5. Mass Spectroscopy				
6. Infrared Spectroscopy	K. A. Saturday		D. Clark	
7. Activation (Neutron, other)				
8. X-ray Diffraction	W. C. Mosley, G. G. Wicks B. Osgood	J. Shackelford		
9. X-ray Fluorescence	D. Johnson			
10. Electron Microprobe	W. C. Mosley P. O'Rourke	H. Green		
11. SEM/EDX	G. G. Wicks E. F. Sturcken	J. Pangbourne		
12. TEM		D. Howitt		
13. STEM	E. F. Sturcken	D. Howitt		
14. Nuclear Mag. Resonance		J. Pangbourne		
15. Radiochemistry				
16. Radiation Shielded or Contained Instruments	XRD (B. Osgood) SEM (J. Congdon) AA Ion Chromotog. Mass Spect.			

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