SPECTRO REPORT

APPLICATION REPORT 93

SPECTRO Analytical Instruments Inc, Fitchburg/USA

ANALYSIS OF CERAMIC MATERIALS BY ICP USING SLURRY SAMPLE PRESENTATION

Introduction

This application report considers the analysis of materials by slurry/ICP, and the benefits that this technique brings to the analyst.

SPECTRO Analytical Instruments has been working on this method for well over a year at Fitchburg/USA, and this paper will be reviewing the advantages and disadvantages, the hardware and operating conditions, and some of the results SPECTRO has obtained from these studies.

Advantages of Slurry Technique

Obviously any new technique must have benefits over existing methods, otherwise it would be of no use to anyone. Most of the sample SPECTRO has looked at have been refractory materials that are very difficult to dissolve. Their analysis requires a trained chemist with plenty of time to get the samples into solution.

The first advantage of slurry ICP is that you save money; the use of expensive laboratory items such as muffle furnaces, platinum crucibles and other assorted equipment is not required, and consumable costs are reduced.

Secondly sample preparation time is considerably shortened, saving many hours and drastically improving turn around time.

Potentially hazardous techniques are eliminated, which not only makes this a very safe technique, but also requires less highly trained personnel.

Disadvantages of Slurry Technique

As with all methods however, there are some drawbacks. Most problems are caused by sample inhomogeneity - notably particle size distribution - and subsequently the different responses within the plasma of the various size particles.

Secondly, solid calibration standards can be very difficult to obtain, it is difficult to run a liquid standard calibration and a slurry sample.

Leaching can be another problem, water soluble salts (such as soda) can leach into the solution and give different responses, also leaching is particle size dependent which can cause more problems.

Hardware Requirements

At this point it is important to consider how to modify the ICP to accept samples in slurry form. The slurried samples requires continous mixing. In the majority of cases a magnetic stirrer is perfectly adequate.

The sample introduction system requires a hardy, unblockable system which will nebulise fairly large particles. In our case this consists of a slightly modified Babington nebuliser, a small volume spray chamber and a wide bore injector tube in the torch to prevent clogging.

Picture 1 shows a diagrammatic representation of the sample presentation system. The sample is mixed with a water and surfactant mixture until a well formed slurry is produced. The sample is agitated continously and is pumped into the nebuliser by a peristaltic pump. The Babington nebuliser used for this technique is modified to handle slurry applications. The spray chamber used is a minimal volume design with no obstructions in the sample path. The torch used is a standard SPECTRO fixed torch with a 1.8 mm ID capillary injector tube.

Operating parameters are essentially the same as those used for conventional aqueous ICP. These parameters are based on a study of alumina standards. Analysis of other slurry materials since this first study confirms these operating parameters.

Slurry/ICP Operating Parameters

Sample delivery rate:	2	ml min-1
Nebuliser flow:	0.7	l min-1
Auxiliary flow:	0.8	l min-1
Coolant flow:	12	l min-1
Observation zone:	15	mm above coil
RF power:	1200	W

Typical Sample Preparation

1. Grind sample to pass 325 mesh
2. Weigh into disposable plastic beaker
3. Add water/surfactant mixture
4. Stirr well
5. Aspirate

Sample preparation is fairly simple, probably the most difficult part is getting a sample uniformly ground to the correct particle size. The sample is then weighed on a top pan balance into a disposable plastic beaker. Accurate weighing is not required as the method uses an internal standard. The water/surfactant mixture is added and the whole mixture is stirred for several minutes before being aspirated. The use of a surfactant is required for two reasons, firstly to act as a dispersant for the slurry to prevent agglomeration, and secondly to stabilise conditions in the spray chamber.

Applications of Slurry Analysis

Some of the materials SPECTRO has worked on for slurry/ICP in the Fitchburg applications laboratory are: Alumina, Zirconia, Glass, Silicon Carbide, Slags, Sands and Aluminium Fluorides. In almost all cases these samples are very difficult to get into solution to run conventionally. Dissolution may require the use of sulphuric or phosphoric acids with the immediate results that neither sulphur nor phosphorous can be read by the ICP. In the case of aluminas, a very lengthy dissolution process can be avoided. In the case of silicon carbide, the dissolution process involves a sodium peroxide fusion, so a potentially hazardous and time consuming technique can be avoided.

In the following text SPECTRO considers some examples, beginning with alumina. This is almost an ideal material to run, it is free flowing, it can be ground to the correct particle size, most of the minor and trace consituents, with the potential exception of the oxides of sodium and calcium, are not prone to leach into the solution (however, in this cases SPECTRO has not seen leaching problems). Well characterised standards are also readily available, they are mandatory for the calibration.

Alumina

- an almost ideal material to run
- 1-10 % (w/v) slurry
- good standards are readily available
- constant matrix.

Picture 2 shows the calibration curve for vanadium oxide in alumina using the Slurry/ICP technique. Some scatter is seen, although the four points all lie on a reasonable line, but this can be significantly improved if an aluminium line is used as the internal standard (see next sections).

Picture 3 shows the improvement seen in the curve of vanadium oxide when an internal standard is used. Similar improvements were seen for all analyte elements. The internal standard used must be in the same form as the sample, in this case it must be in the slurry. Liquid additions of standard solutions do not work well. In the case of alumina we can use Al 266.9 nm as the internal standard.

The following table shows the BEC and DL values in the solid for alumina. The data is expressed in µg g-1 for a 20% (w/v) slurry. The standard deviation used in the circulation for the DL is from 10 integrations. The values approximate those achievable with a 5% (w/v) alumina solution, but are obtainable in minutes (literally).

Detection limits observed for alumina matrix by slurry/ICP

Element	Line (nm)	BEC (µg/g)	DL (2 s) (µg/g)
Fe	259.940	5.0	0.1
Si	288.158	24	0.7
Ti	337.249	3.5	0.08
V	292.402	5.8	0.1
Ca	317.933	7.3	0.1
Na	589.595	13	0.2

A NIST standard was run as an unknown against the slurry calibration and the values here show the slurry technique results to be very good. A couple of points to be noted here are the very small deviation of the slurry results indicating this method has very good precision, and also the very good agreement between the certified and found values. It is interesting to note that we have slightly lower values than the standard for some of the oxides, and these lower results have been confirmed by outside laboratories using conventional techniques.

Analysis of NIST SRM 699 Reduction Grade Alumina

Element line (nm)	Certified value (% oxide)	Found value (% oxide)
Fe 259.940	0.013 +/- 0.002	0.011 +/- 0.0002
Si 288.157	0.014 +/- 0.001	0.012 +/- 0.0002
V 292.402	0.0005 +/- 0.0002	0.0006 +/- 0.00005
Ca 317.933	0.036 +/- 0.002	0.033 +/- 0.0008
Ga 294.364	0.010 +/- 0.01	0.011 +/- 0.0005
Na 589.595	0.59 +/- 0.01	0.59 +/- 0.008

Silicon carbide

- An almost ideal material to run
- Mean particle size 3 micron (µm)
- Simple background spectrum
- Standards are available
- Constant matrix

In the following text another matrix, silicon carbide, is considered. Again this is an almost ideal material to run, the mean particle size of 3 microns means the material slurries exceptionally well. It has a fairly simple background spectrum, the matrix is constant and standards are well characterised and readily available.

Picture 4 shows the calibration curve of calcium 317.933 nm in silicon carbide. Silicon 256.864 nm is used as the internal standard. The plot of ratio concentration against ratio intensity shows a good curve fit with very little scatter.

The following table shows the elements analysed in the silicon carbide slurry and shows the precision values expressed in percent relative standard deviation for 10 consecutive integrations. The precision is reasonable, and much better than would be expected. These elements are all at minor or trace levels 0.1 to 0.01 % in the solid.

Precision of Silicon Carbide

Element	Line (nm)	Precision (% RSD)
Si	256.864	1.3
Fe	259.940	1.3
Al	308.215	1.2
Cu	324.754	0.8
Ni	231.604	1.5
V	292.402	2.1
Cr	267.716	0.9
Ti	334.941	2.1
Ca	317.933	2.0

The table on the following page shows the detection limits (in µg/g of the solid sample) in the silicon carbide matrix. This is calculated from a 10 % w/v slurry solution.

Detection Limits of Silicon Carbide

Element	Wavelength (nm)	DL (2s) (µg/g)
Fe	259.940	0.2
Cu	324.754	0.2
Ni	231.604	0.6
V	292.402	0.5
Cr	267.716	0.1
Ca	317.933	0.04
Ti	334.941	0.08

Zirconia

- Can be finely crushed to -325 mesh
- Complex background spectrum
- Constant matrix
- Some standards available

Zirconia (zirconium oxide) is another difficult material to analyse by conventional wet techniques. It slurries very well as it can be easily ground to the required particle size. It has a basically constant matrix and some standards are available. However, it does have a complex background spectrum, so line selections has to be made very carefully. Picture 5 shows the calibration curve of Al 308.215 nm in zirconia, again a very good correlation can be seen. In this example zirconium 278.32 nm is used as the internal standard.

The next table lists the elements and wavelength used in the analysis of zirconia by slurry/ICP. The right hand column shows the typical precision obtained from 10 consecutive integrations. These results are from a typical production sample containing 0.1 to 0.001 % of the oxides in the solid. An interesting thing to notice here is that all the wavelengths used are common analyte lines, so exotic lines did not have to be used despite the complex background spectrum.

Precision (Zirconia)

Element	Wavelength (nm)	Precision (% RSD)
Si	288.158	1.48
Al	308.215	1.51
Ti	334.940	1.20
Mg	279.079	1.31
Fe	259.940	1.54
Ca	317.933	1.93

Titania Mineral Sand

- Difficult material to run
- Matrix is not constant
- Complex background spectrum
- Very few standards available

This is another material that presents analysts with problems when using conventional techniques. Titania mineral sand is used as a raw product in the abrasives industry. The matrix varies considerably, with widely varying amounts of titanium, iron and aluminium oxides. There are very few certified standards available and the background spectrum is very complex.

Picture 6 shows the calibration curves for manganese and niobium. Both plot extremely well, giving good calibration points. Interestingly enough the internal standard used was vanadium (311.071 nm). Vanadium is present in this material as a minor, and it was chosen because it was almost constant in all standards and samples. Alternatively titanium could have been used with matrix correction.

However, from the following data can be seen how well the vanadium internal standard worked. The certified values are of an in-house QC sample from the customer, and we see excellent agreement between the results. As dissolution of this type of material can be extremely problematic, it is gratifying to see good results from a method where the sample took literally a few minutes to prepare, and gives the analyst an easy, fast alternative to conventional techniques.

Analysis of Standard Material (Titania Mineral Sand)

Element	Certified	Found
Al_2O_3	0.81	0.87
Fe_2O_3	11.2	11.7
Nb_2O_5	0.398	0.38
P_2O_5	0.185	0.18
MnO	0.38	0.38

The elements of interest and the wavelengths used in the analysis of titania mineral sand are shown in the following section. Precision is excellent, the values here are calculated from 5 consecutive integrations of a 1 % w/v slurry.

The line selection is interesting, iron and manganese are not typical aqueous lines which because of the complex background spectrum cannot be used.

Precision (Titania Mineral Sand)

Element	Wavelength (nm)	Precision (% RSD)
Al	308.215	1.14
Fe	273.074	0.48
Nb	316.340	1.03
P	178.287	3.10
Mn	280.106	0.69

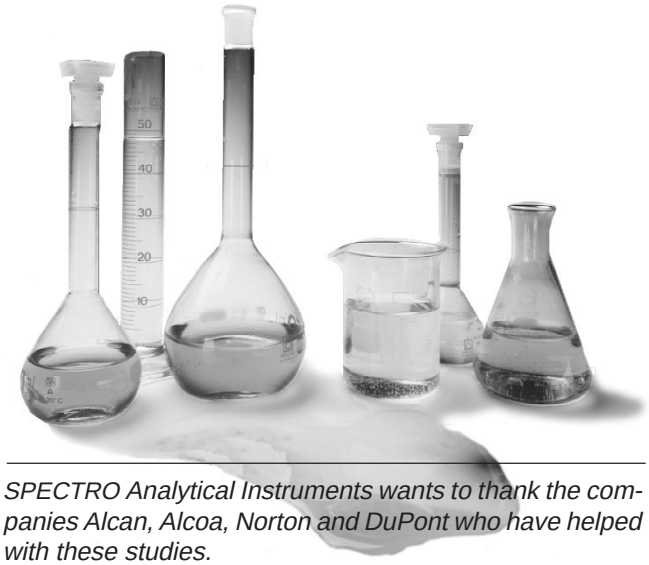
Conclusions

- Technique works well
- Difficult analysis made easy
- Simple method
- Requires care in method development

In conclusion, slurry analysis technique works very well. A large number of different material types have been studied and slurry/ICP works for most of them.

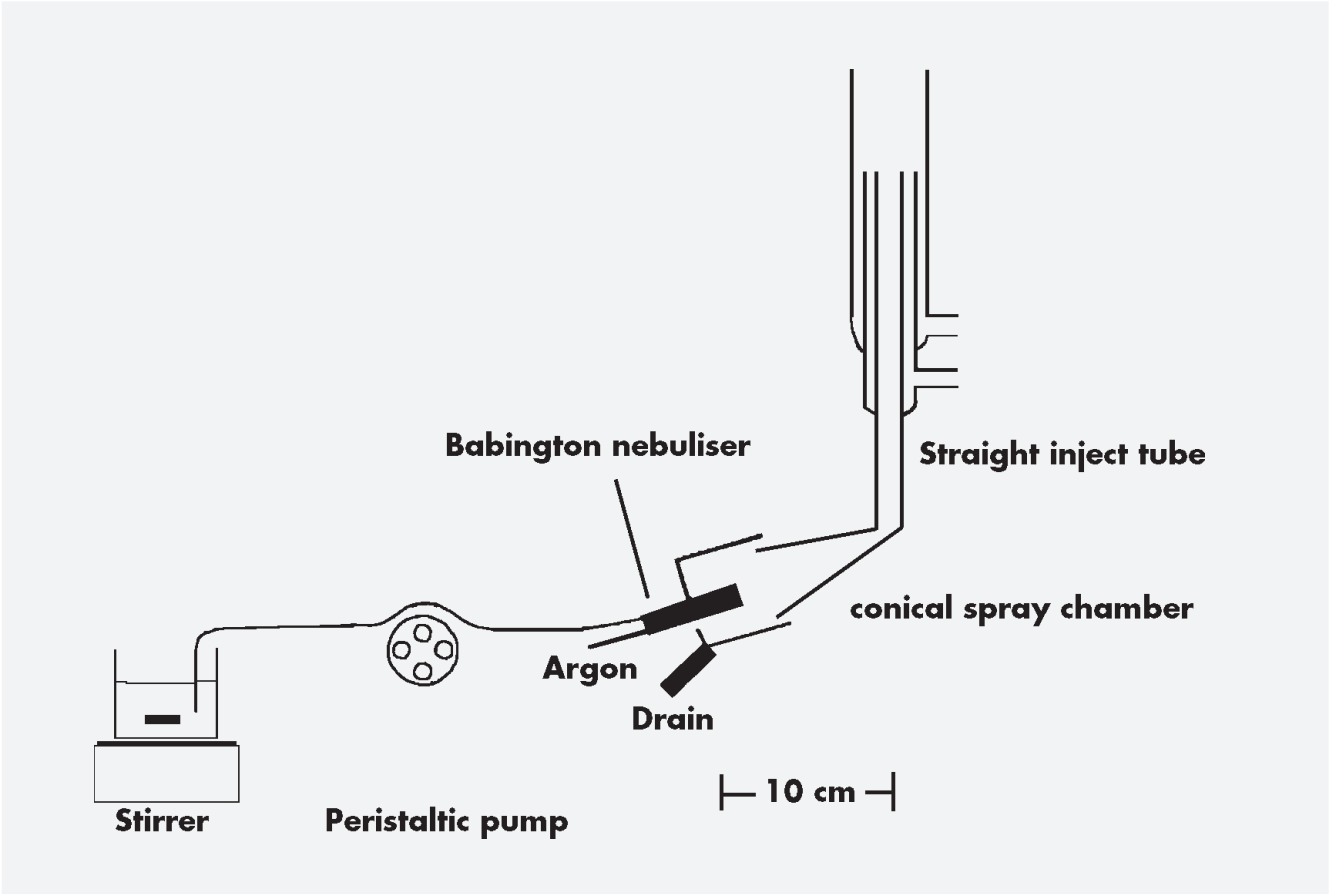
Samples which are difficult to dissolve, assuming they can be ground fine enough, are easy to analyse. The method is very simple and is currently being used in some production facilities, which is a feat in itself!

The initial method development does require much thought, however, careful line selection and choice of an appropriate internal standard will remove most obstacles. ■

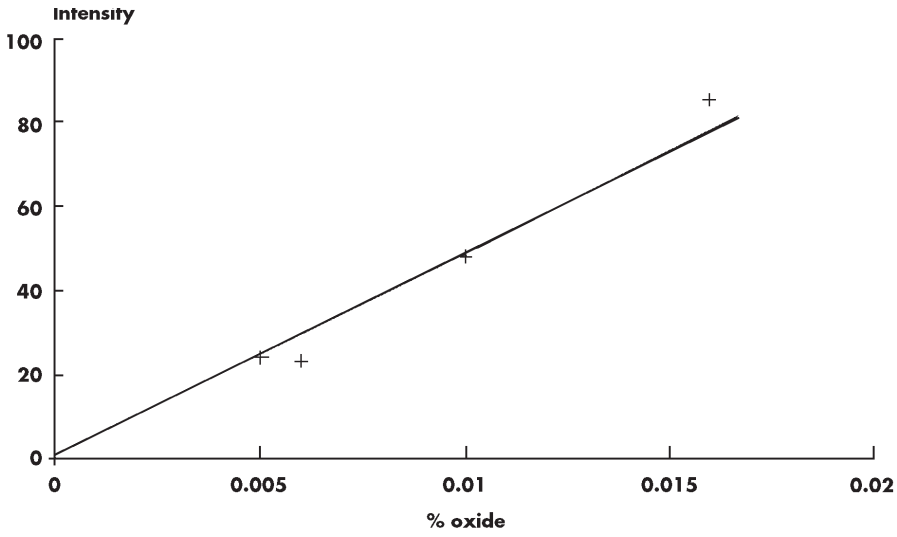


SPECTRO Analytical Instruments wants to thank the companies Alcan, Alcoa, Norton and DuPont who have helped with these studies.

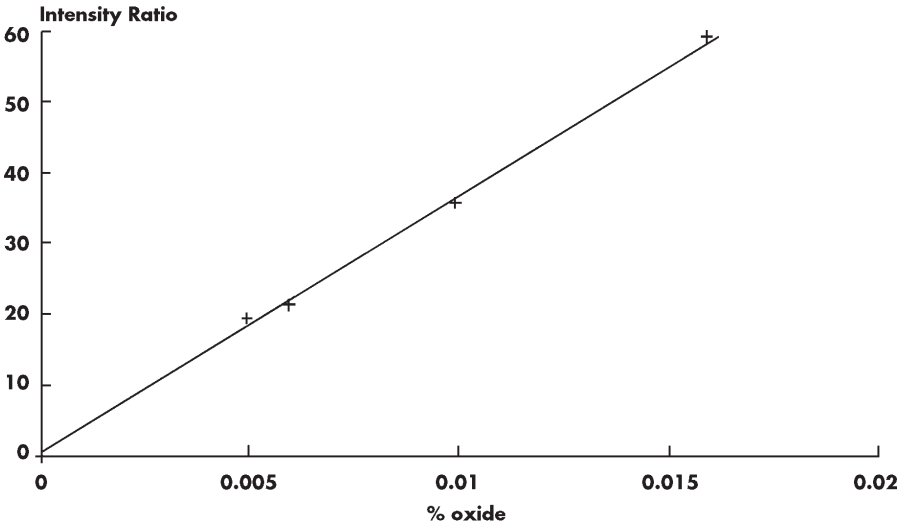
Picture 1: Sample Presentation System for Slurry/ICP



Picture 2:
Calibration Curve for V 292.402 nm in Alumina by Slurry/ICP

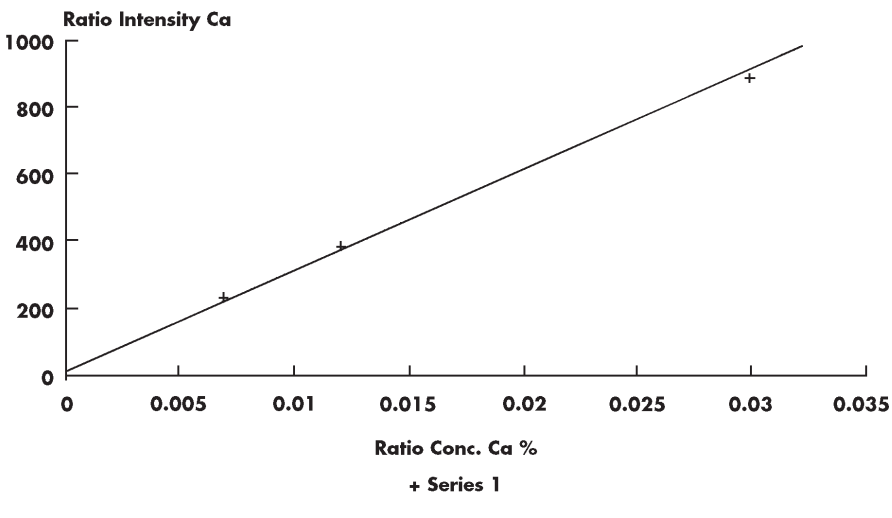


Picture 3:
Calibration Curve for V 292.402 nm in Alumina by Slurry/ICP



Al 266.917 nm internal standard

Picture 4:
Calibration Curve for Ca 317.933 in Silicon Carbide jby ICP/Slurry



Si 256.864 nm internal standard

Figure 5:
Calibration Curve for Al 308.21 in Zirconia by Slurry/ICP

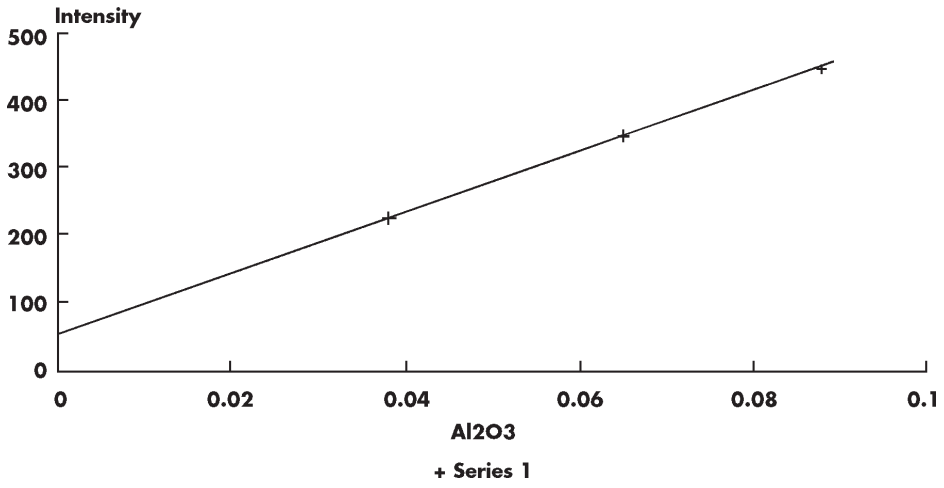


Figure 6:
Calibration Curves for Mn and Nb in Titania Mineral Sand by Slurry/ICP