INORGANIC ANALYSIS OF SOLIDS BY LASER ABLATION INDUCTIVELY COUPLED PLASMA-SOURCE MASS SPECTROMETRY

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ABSTRACT:

Use of a laser for solid sample introduction to an inductively coupled plasma (ICP) mass spectrometer is described. The effect of free-running laser pulses on metals, as revealed by scanning electron microscopy (SEM), is outlined. System optimization is sketched, and the use of the technique illustrated by the analysis of four nickel-base alloys.

1. INTRODUCTION

Inductively coupled plasma-source mass spectrometry (ICP-MS) combines the advantages of a plasma as an ion source with the sensitivity of mass spectrometry, to give rapid multielemental analyses and isotope ratio measurements |1,2|. Sample digestion, using methods adapted from ICP-atomic emission spectrometry (ICP-AES), is generally employed and the samples introduced to the ICP by pneumatic nebulization. Occasionally ultrasonic nebulizers, which should be more efficient, are used. Such methods have proved successful for the analysis of a great number of sample types, calibration against aqueous standards being possible.

However, digestion has associated problems: some matrices are very difficult to dissolve; hazardous reagents often have to be handled; volatile elements may be lost; sample contamination may occur; digestive reagents may contain elements which cause spectral interferences. Not least, many hours may be spent in sample preparation. For example, the marine biological reference materials, dogfish liver tissue (DOLT-1) and dogfish muscle tissue (DORM-1), were prepared by Beauchemin et al |3| using the following procedure. Weighed samples were heated for two hours in conc. nitric acid, the resulting mixtures refluxed for several hours, evaporated to dryness, left to cool, redissolved in nitric acid and hydrogen peroxide, and so on. Clearly,

this digestion procedure requires at least a full day's work.

Such difficulties are responsible, at least in part, for the search for alternative sample introduction methods. Motivation also comes from users with specific interests such as the analysis of microliter sample volumes or the determination of elements in rock inclusions. Finally, from a historial perspective the application of various sample introduction technologies to ICP-MS seems a logical extension of the use of such systems in combination with other analytical techniques, particularly ICP-AES.

Amongst others, flow injection |4|, electrothermal vaporization |5| and laser ablation |6| have been used with ICP-MS. Laser ablation is particularly attractive since no sample preparation is necessary, spacially-resolved information can be obtained, and interferences are reduced in the "dry" plasma. However, the analytical difficulties of obtaining accurate, fully quantitative analyses by LA-ICP-MS are also well known. These relate primarily to the dependence of the laser-solid interaction on many factors, including on the one hand, the wavelength, energy and mode of the laser, and on the other, the nature of the sample surface and the thermal properties of the sample matrix.

In this work some fundamental studies of the nature of the ablated material using SEM are discussed. Optimization of the LA-ICP-MS system is outlined. Four standard alloys are analyzed to illustrate use of the technique.

2. LA-ICP-MS SYSTEM

A J.K. 2000^{TM} ruby laser was used for sample ablation with ionization and detection by the Surrey prototype spectrometer |7|. Free-running or Q-switched pulses in the energy range of

about 0.01 to 1.5 J could be produced at a rate of up to one per second. Details of the laser and the ablation cell are essentially those given by Gray |6|, with some modifications as reported by Durrant |8|. Figure 1 shows the laser, ablation cell and associated gas lines. The laser could be fired onto the sample which was mounted on the turntable within the cylindrical borosilicate glass cell. Degree of rotation of the turntable between individual shots could be controlled so that optimum distance between ablated pits could be set up. An immediate or delayed trigger of the accumulation of a spectrum could be initiated by the first laser pulse. The cell was fed with argon and a separate "add-in" flow joined the outflow of the cell beyond the two-way valve. Use of such a flow ensures an uninterrupted supply of argon to the central channel of the ICP, even if the cell flow is shut off.
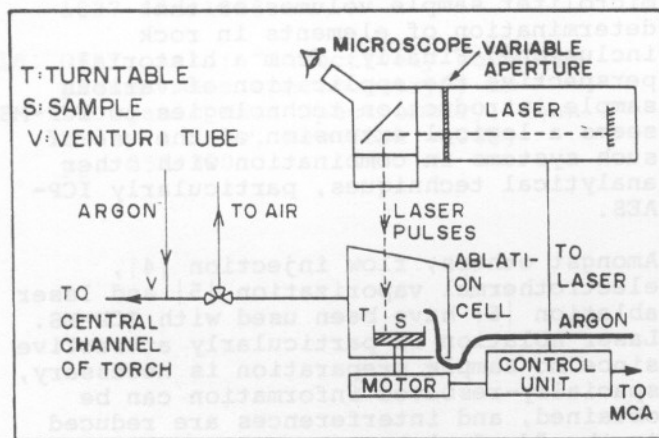

Fig. 1 - Laser ablation system.

Free-running rather than Q-switch pulses are generally used for analysis. Q-switched pulses deliver energy in a giant pulse, or a few giant pulses, whose duration is several microseconds. Giant pulses might be expected to give better analytical performance since they produce very rapid heating and minimize differential vaporization between elements. However, this is at the expense of sensitivity; normal mode pulses being typically about 40 times more effective per unit energy in this regard |8|. Moreover, Q-switched pulses give increased background levels; possibly because of the very rapid expansion of gas in the ablation cell, the disturbance being visible in the first vacuum stage of the spectrometer. This expansion may resuspend matter deposited along the gas lines and so cause the rise in the background levels observed.

3. NATURE OF ABLATED MATERIAL

Metals, being relatively homogeneous, are an obvious test material for analysis by LA-ICP-MS. Therefore the nature of the material ablated from metals is of particular interest. Here, the ablation of metal was investigated using free-running pulses. SEM was used to observe the surface of the ablated sample and ejecta collected on a filter.

Nickel of about 99% purity, in the form of a coin-sized disc (ϕ = 32 mm), was ablated with N mode pulses. Weighing the disc before and after many hundreds of shots, produced the data shown in Fig. 2. The ablated mass shows an approximately linear relationship with laser energy. Such curves are useful for the estimation of absolute detection limits.
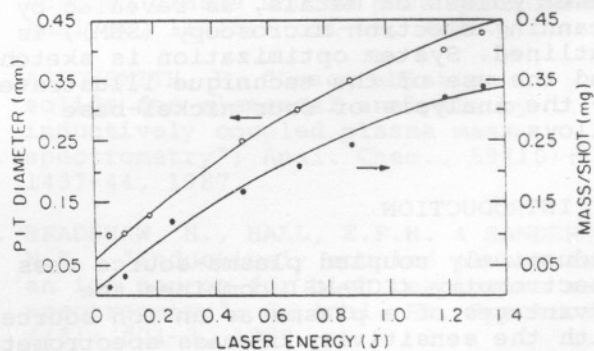

Fig. 2 - Ablated pit diameter and ablated mass as a function of N mode laser energy. Sample was a nickel disc.

Deep, well-defined circular pits are produced; the pit diameter, which was determined under an optical microscope, showing a similar form of relationship to that exhibited by the ablated mass. The literature reveals similar relations for metals. Manabe and Piepmeier |9|, for example, reported similar curves for the ablation of pure copper and National Institute of Standards Technology (NIST) steel.

A scanning electron micrograph of the surface of the nickel disc which had been ablated by a 0.3 J N mode shot revealed a pit diameter of about 170 μm. A cross-section of the same pit prepared by mounting the sample in a resin and carefully abrading the surface, allowed the measurement of the pit depth, which was about 700 μm. The ablated mass was calculated at between 0.05 mg and 0.14 mg, assuming a cone or a cylinder for the ablated volume respectively. This is in approximate agreement with the mass

obtained by weighing. Cracks in the pit wall, particularly near the pit bottom, were also observed, and may be due to the effects of thermal shock.

A millipore filter was placed in the gas flow at the mouth of the ablation cell. Ejecta thus collected were revealed to be spherical droplets (0.1 µm < ∅ < 10 µm). This is in agreement with previous work |10|, and indicates that the greater part of the removed material is melted rather than vaporized. These results are also similar to those obtained in a very recent study by Thompson et al |11|. In the same work, the authors suggested that in the ablation of pyrite (FeS_2) using laser pulses the S:Fe ratio is decreased at low (< 4 µm) particle diameters. It was further proposed that in the ablation of stainless steel the smaller diameter droplets exhibited enhanced Cr:Fe ratios and that elements such as Mn and Mo showed similar tendencies. The data were obtained by energy dispersive x-ray analysis (EXD) with ablation by a ruby laser in the free-running mode at one joule. If correct, this could explain some of the calibration difficulties experienced in LA-ICP-MS. However, the measurements are subtle, depending on the determination of differences in percent levels of elements within volumes of a few cubic micrometers. It would be very interesting to see these data confirmed by other means. In addition, this work raises the question of why good quantitative analyses of metals have already proved possible |12|. To what extent then, does the enhancement effect depend on the matrix composition? Also, is the effect energy dependent? In the author's experience for example, 1.0 J is a high energy for the analysis of metals. Would ablation with 0.1 J shots be subject to the same sensitivity enhancement?

Free-running pulses (0.3 J) normally incident on a rock sample (Canadian Certified Reference Material Project, SY-3) resulted in wider but shallower pits than observed with metals. SEM also revealed melting of parts of the crater wall, indicating that some of the ablated material was removed in the form of microdroplets.

Only droplets of diameter of a few µm or less will be borne by the argon cell flow to the ICP. The size distribution is biased towards such droplets |11|, but unfortunately the relatively few droplets of greater diameter represent a high proportion of the ablated mass. If the proportion of small diameter droplets could be increased, this would lead to greater sample transport to the ICP and therefore also to greater sensitivity. Vaporized material is thought to be very

efficiently transported but probably forms only a minor proportion of the ablated material for N mode pulses.

4. SYSTEM OPTIMIZATION

In solution nebulization ICP-MS the ion optics may be optimized from the respective responses to a standard solution. Typically, for example, using a VG Plasmaquad^{TM} under normal operating conditions, the fully ionized monoisotopic element (^{59}Co) gives a count rate of about 10^5 counts per second at a concentration of 1 µg mL^{-1}. However, in LA-ICP-MS sample material is not fed continuously to the ICP. So to optimize the ion optics the ^{12}C signal is used. This is possible since there is sufficient CO_2 present in the plasma from entrainment and desorption from the walls of the ablation chamber and gas lines. This method is found to give the same optimal conditions as using an element from a repeatedly ablated sample |8|.

The system response depends on the laser, sample and spectrometer parameters. Integrals increase, for example, with increasing mass transfer to the ICP. Mass transfer rate depends on the laser energy, mode and polarization, the sample characteristics (surface morphology, thermal conductivity) and the argon flow through the ablation cell.

Each matrix requires optimization since its ablation characteristics are unique. Optimization is thus very time-consuming. Some systematic investigations |8| have suggested that the conditions given in Table I are reasonable choices; based on sensitivity and signal to background ratios. The laser energy and frequency of shots are determined empirically to give "reasonable" sensitivity. Considerations used when deciding these parameters include: (a) avoidance of plasma saturation-when the rate of arrival of sample material is so high that the ionization process is disturbed; (b) avoidance of the saturation of individual masses of monoisotopic elements, if such elements are to be analyzed; (c) achievement of high S/B ratios.

Experience shows that for most matrices, many lower energy (< 0.3 J) N mode shots are preferable to a few high energy pulses. The advantage of this is a smoother supply of analyte to the ICP. Faster scan times than are used than is typical in solution nebulization work. This is because the count rate is not constant with time and this could lead to counting errors with a slow scan.

TABLE I. System parameters for
multielemental analysis

Spectrometer: Surrey prototype ICP-MS

Plasma Conditions
Coolant Flow   14 Lmin^{-1}
Cell Flow   0.8 Lmin^{-1}
Add-in Flow   -
Forward r.f. Plasma Power   1500 W
Reflected Power   < 20 W

Interface
Load coil - Extraction Aperture
          Separaton   10mm
Extraction Aperture Diameter   1.0mm
Skimmer Aperture Diameter   0.7mm

Ion Optics
Optimized on ^{12}C

Laser
J.K. 2000^{TM} ruby
Ten 0.1J N mode shots per thirty second
         integration

Scan Details
M/Z 4 to 240
Dwell Time per Channel   50 µS
Channels per Sweep   2048
Sweeps per integration   300

5. ANALYTICAL PERFORMANCE

A significant advantage of laser ablation
is the reduction in sample preparation
time. The importance of this depends on
the material to be analyzed since
solution preparation times are strongly
matrix dependent. Sample throughput is
similar or superior to that achieved with
sample introduction by solution
nebulization.

Depending on the matrix, detection limits
are in the range 0.01 to several tens of
µgg-1 |6,8,13|, considerably poorer than
in solution nebulization ICP-MS. In the
latter, however, sample dilution by a
factor of 10 to 10^3 is usually necessary.
It is encouraging that the linear dynamic
range covers at least four decades |8|.

Levels of interferences are also
considerably reduced in the dry plasma
|8,13|; the analytical advantage realized
depending also on the sensitivity. This is
an area worthy of further study.

6. METALS ANALYSIS

Metals are difficult to analyze by
conventional pneumatic nebulization ICP-MS
since hazardous high temperature
dissolution methods using acids such as
conc. HNO_3 and HCl are needed. Analytical
problems are also encountered with
suppression, oxide interferences, and the
extreme concentration range (trace to

percent). For example, matrix effects due
to iron necessitates the use of internal
standardization in the analysis of steels
|14|. Also, in the analysis of nickel-base
alloys a number of oxides have been found
to lie at masses of interest viz $^{53}CrO^+$ on
$^{69}Ga^+$; $^{59}CoO^+$ on $^{75}As^+$; $^{95}MoO^+$ on $^{112}Cd^+$ |15|.

In view of these difficulties, it is
interesting to see the feasibility of the
analysis of metals by LA-ICP-MS. Here,
four nickel-base alloys have been analyzed:
British Chemical Standard (BCS) 346; NIST
897, 898 and 899. No sample preparation
was necessary, except that some of the
metals were in the form of chips and had
to be pressed into freestanding pellets.

TABLE II. Analysis of Nickel Alloys by
LA-ICP-MS (concentrations in
w/w %).

| | BCS Nickel Alloy 346 | | NIST Nickel Alloy 897 | |
Element	LA-ICP-MS	Inf.*	LA-ICP-MS	Inf.
B	0.02	-	0.04	0.01
Al	6.42	5.5	2.31	2.00
Ti	6.91	5	2.53	2.00
V	1.25	1	-	-
Cr	10.9	10	10.8	12
Co	16.3	15	11.3	8.5
Zr	0.05	-	0.10	0.10
Mo	3.94	3	2.11	-

| | NIST Nickel Alloy 898 | | NIST Nickel Alloy 899 | |
Element	LA-ICP-MS	Inf.	LA-ICP-MS	Inf.
B	0.02	0.01	0.01	0.01
Al	2.33	2.00	1.96	2.00
Ti	2.38	2.00	2.04	2.00
V	-	-	-	-
Cr	10.4	12.0	8.7	12.0
Co	10.9	8.5	9.8	8.5
Zr	0.09	0.10	0.10	0.10
Mo	1.95	-	1.79	-

*Information value

The data (Table II) were calculated from
the elemental concentrations certified in
BCS nickel alloy 345 without internal
standardization. Ten 0.1 J N mode shots
were used per integration. Fair agreement
between the LA-ICP-MS and information
values is apparent. Differences may not be
wholly attributable to errors in the
LA-ICP-MS data since the NIST values are
not rigorously determined, but are
information values only.

7. CONCLUSIONS

Free-running pulses from a ruby laser
produce well-defined pits in metals; the
bulk of the material being ejected as
molten drops. Such N mode pulses are
of prime interest for the mobilization of
sample material for introduction to the

ICP because of the good sensitivity per unit laser energy associated with them.

System optimization depends on many parameters related to the laser, sample and spectrometer. However, with the exception of the mass scan rate (faster) and plasma power (higher), optimal conditions are similar to those used in solution nebulization ICP-MS.

For the analysis of metals most of the anticipated advantages are realized in practice. In particular, virtually no sample preparation is necessary. A brief illustration of the power of the technique has been given by the determination of eight elements in four nickel-base alloys. Certainly LA-ICP-MS shows promise as a means of rapid multielemental analysis.

Avenues of possible development include: (1) study of the ablation process and its influence on quantitative analysis; (2) the investigation of a wide range of sample types; (3) the development of artificial standards; (4) the development of alternative calibration procedures; (5) exploitation of the technique's microprobe capability; (6) further improvement in analytical performance by addition of molecular gases to the argon coolant or central channel flow.

8. ACKNOWLEDGMENTS

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