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Application of Laser Ablation ICP-MS to Elemental Analysis of Glasses

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Abstract. A technique involving the coupling of laser ablation and inductively coupled plasma mass spectrometer has been used for semi-quantitative analysis of glasses without sample dissolution. The characteristic features of this technique is low detection limit and accuracy between a few % up to 20%. An NIST glass standard (SRM 612) was dissolved and then analysed by ICP-MS in semi-quantitative mode. The results were in close agreement with the certified values for elements such as Mn, Sr, Y, Ti...

Key words: inductively coupled plasma mass spectrometry, laser ablation, semi-quantitative analysis, glasses.

Abbreviations

AA: atomic absorption
ICP-OES: inductively coupled plasma optical emission spectroscopy
ICP-MS: inductively coupled plasma mass spectrometry
LA: laser ablation.

Well established analytical techniques, like inductively coupled plasma optical emission spectroscopy, polarography, atomic absorption with electrothermal vaporisation have reduced the detections limits in elemental analysis down to concentrations of 1 μg/l or below, depending on the techniques and the elements under investigation. Although reasonable results may be obtained these techniques are slow and an often complex wet chemistry treatment is a necessary prerequisite. More recently the introduction of ICP-MS (inductively coupled plasma-mass spectrometry) resulted in a major improvement elemental analysis because of the following advantages: (a) It allows a wider range of elements to be studied, in comparison to AA, ICP-OES and polarography, are more limited; (b) In general, detection limits for most elements are lower than those of most others techniques; (c) The analysis time for the full elemental coverage is shorter than the fastest of the other used techniques (ICP); (d) The sensitivity is broadly uniform, enabling the analyst to use only one standard for semi-quantitative analysis; (e) The semi-quantitative mode in ICP-MS give results whose accuracy vary from a few % up to 20% maximum in solution.

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However, commonly use of ICP-MS is limited to liquid samples and it is well known that the accuracy of the results largely depends on the sample decomposition step. Therefore the direct atomisation of solid samples by using laser ablation is very attractive [1, 2] because of the elimination of the errors due to sample preparation (contamination, losses....) and an increased analytical throughput. However, the major disadvantage of LA-ICP-MS is calibration. The best method to calibrate analysis in LA-ICP-MS is the use of matrix matched homogeneous standards incorporating an appropriate internal standard. But this case represents the ideal solution and it is rarely possible to achieve this for practical analysis.

Two strategies may be employed in order to achieve a semi-quantitative analysis of a given solid sample by LA-ICP-MS. The best solution is to use the known concentration of a suitable analyte (determined by another analytical technique) as an internal standard for the quantification against an instrument response curve. In order to obtain an adequate coupling between the laser and the sample for analysis of powders it is necessary to produce a pressed powder pellet with a suitable binder, this affords an opportunity for the incorporation of an internal standard (e.g. In_2O_3) with the binder [6, 7]. However the precision of this method is limited by the homogeneity of the distribution of the internal standard within the pellets.

The second approach is to use a minor abundant isotope of a matrix element as an internal standard however this assumes that this species is homogeneously distributed throughout the sample and the analyte response is similar to a reference material used for calibration. This approach is useful for intercomparison of sample with similar matrices but the accuracy is limited to a factor of 2 to 3 [8] since matrix effects between sample and the calibrating standard cannot be taken into account.

Two methods are available for more quantitative analysis by LA-ICP-MS:

External calibration against matrix matched standards. It is necessary to know the composition of the matrix precisely and it is very time consuming for complex matrix.

The second possibility is a comparison with reference standards when these standards are available. In the case of glass samples analysis by LA-ICP-MS there is no problem with the homogeneity of the sample and a minor isotope of the matrix (Si) can be used as an internal standard Si^{29}.

Experimental

Solid Sample Analysis by LA-ICP-MS

A laser beam is focused on the sample [3]. At the focus point the energy is so high that an ablation mechanism [4] occurs which generates micro-particles of the analysed material. These are carried by an argon stream to an inductively coupled plasma (ICP), where they are atomised and ionised.

A portion of these ions is sampled through an interface maintained at low pressure and passes through a series of electronic lenses to be focused on the entrance slit of the quadrupole analyser. Then the ions are transmitted according to their mass to charge ratio to the detector and detected through a continuous dynode electron multiplier operated in the pulse counting mode. The signal is amplified and measured (see Fig. 1).

Instrumentation

Laser ablation ICP-MS system: The instrument used in this study is a VG PLASMAQUAD II+ (VG ELEMENTAL), including a laser ablation device (VG LASERLAB). This laser ablation system

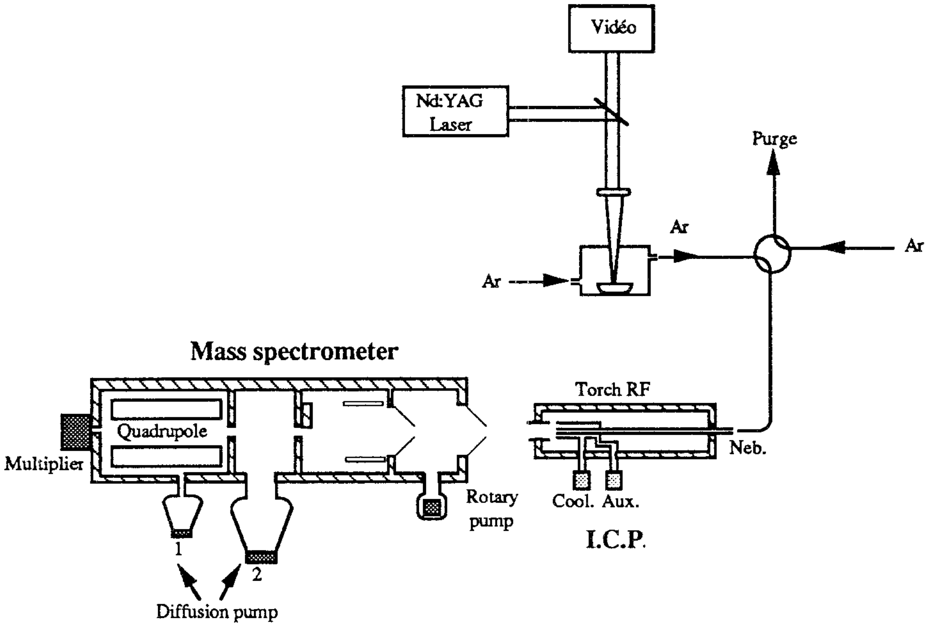

Fig. 1. Instrument

Table 1. Operating conditions for the laser

Fundamental wavelength	1064 nm
Mode	Q-Switch
Power beam	80 mJ
Defocused beam	1.5 mm
Repetition rate	15 Hz
Sampling	1 point
Analysis time	1 minute

consists of a xenon flash lamp, pumping a Nd:YAG rod, permitting the laser emission at the fundamental wavelength of 1064 nm. The laser can work either in free-running or in Q-switch mode with a maximum repetition rate of 15 Hz with a maximum power of 680 mJ and 250 mJ respectively. The laser beam is reflected at 90° and pass through a lens with a focal distance of 75 mm, and then in a quartz cell which contains the sample. The sample is then vaporised and rapidly condensed to form an aerosol (or micro-particles) which is carried by an argon stream to the torch. Two stepper motors allow to shift the cell under the laser beam. The operating conditions of the laser and the ICP-MS are given in Tables 1 and 2 respectively.

Glass Samples Preparation

The conventional ICP-MS methods require liquid samples, then after grinding the sample to less than 80 μm, an acid attack is performed with the following mixture: nitric acid + hydrofluoric acid + perchloric acid. The solution is carefully heated in order to avoid the evaporation of some elements forming volatile species (e.g.: Sn, Cr). The following details are pertinent:

— sample weight 500 mg of glass finely ground
— acid attack: 2 ml HNO_3/4 ml $HClO_4$/5 ml HF

Table 2. Operating conditions for the ICP-MS

Incident power	1350 W
Reflected power	<5 W
Coolant flow	14 l/min
Auxiliary flow	1 l/min (nebulisation) 0.5 l/min (laser ablation)
Nebuliser flow	0.86 l/min (nebulisation) 1.1 l/min (laser ablation)
Sample uptake rate	0.8 ml/min (nebulisation)
Channel number	2048
Scan number	100
Dwell time	160 μs
Detection mode	pulse counting

- — evaporation of acids (carrying not totally to dryness)
- — recovery in 2 ml of HNO_3 and adjusting in 50 ml flask after adding 50 μl of indium at 100 mg/l (internal standard in ICP-MS), with a final concentration of 100 μg/l in indium. (The same solutions are used for determination in ICP-OES and ICP-MS).

When the analysis is carried out using laser ablation, no chemical preparation is required. The sample is only cut into small pieces and inserted in the ablation chamber.

Results and Discussion

In ICP-MS the semi-quantitative analysis of mineralized samples solutions is based on the instrumental response curve determined from a solution containing ten elements at the same concentration of 100 μg/l. The internal standard which is used afterwards is indium-115. In LA-ICP-MS the NIST 612 glass standard is used to determine the responses versus mass curve. The list of the elements and the response curves are shown in Figs. 2 and 3.

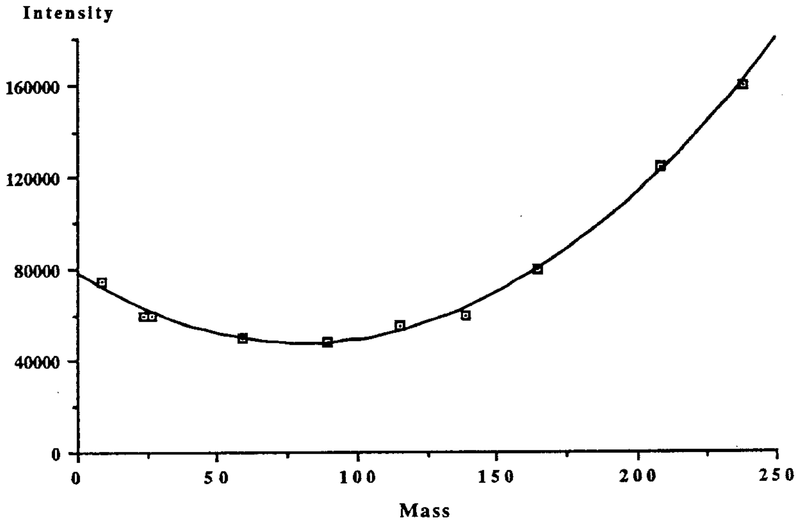

Fig. 2. Response curve in conventional nebulisation. Elements list: Be, Mg, Al, Co, Y, In, La, Ho, Pb, U

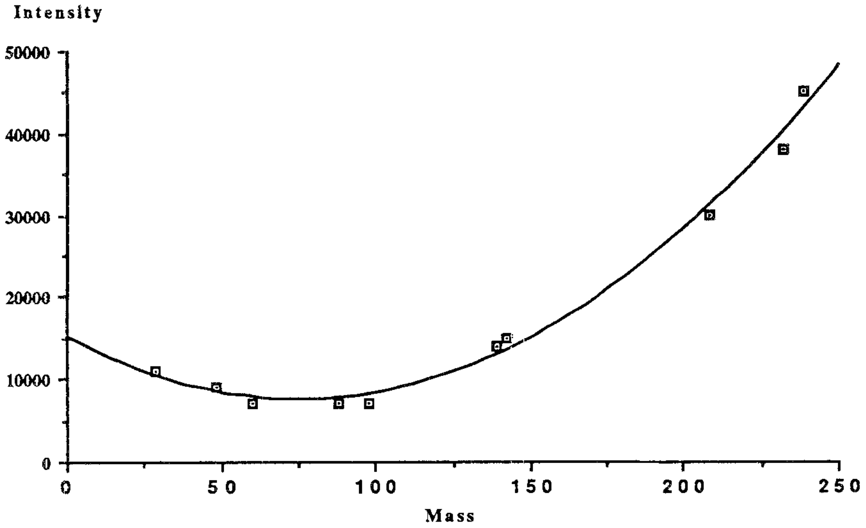

Fig. 3. Response in laser ablation from NIST 612 glass standard. Elements list: Si, Ti, Ni, Mo, Sr, La, Ce, Pb, Th, U

These two response curves have similar shape and the form of the curve has been constant for the past three years. However, variations are seen in the response from day to day due to changes in optics, plasma power or multiplier gain. A recalibration is made every half day to correct for the instrument drift in a day.

In order to check the validity of our digestion method and the reproducibility of the assays, four powdered aliquots of a reference material NIST 612 glass were dissolved, and the resulting solutions analyses by conventional ICP-MS. The average deviations between certified and measured values is 15% in ICP-MS with conventional nebulisation (semi-quantitative mode), for elements like Mn, Ba, Ca, Pb, Ce, Ti, etc ... (see Table 3).

This study shows that the dissolution method used is suitable for the elements investigated. Using the NIST 612 glass for instrument calibration we have analysed ten glasses referenced 1 to 10. The indicative values and those obtained by laser and mineralisation are given in Tables 4–9 for the elements Ti, Mn, Zr, Ba, Pb, Sr, Cu and three rare earths (La, Ce, Y). The indicative values are determined by XRF and by ICP-OES after mineralisation. The laser Q-switch mode is used because of a much better coupling with glass sample than the free-running mode. At the wavelength of the laser the glass samples are transparent and frequently the ablation process occurs on the support and not on the sample. To avoid this limitation the laser beam is focussed 1.5 mm above the target which produces a micro-plasma on the surface of the sample and gives rise to the ablation mechanism.

In Table 4, the results obtained for titanium present at high concentration in the glass samples are shown. For all sample there is a good agreement between the indicative values, those obtained by LA-ICP-MS and solution analyses except in laser ablation for sample 9, with errors of about 30%. Results on trace elements (concentration rage: 10 to 100 $\mu g \cdot g^{-1}$) are given in Tables 5 to 7. There is also a good agreement between the different series of results for each element. Furthermore, the linear range extend up to 2000 $\mu g \cdot g^{-1}$ for manganese.

Table 3. Solution analyses of SRM 612 ($\bar{X}$: mean of 4 independent analyses)

Element	Certified ($\mu g \cdot g^{-1}$)	ICP-MS$_{(SQ)}$ ($\mu g \cdot g^{-1}$)
Mn	40	$\bar{X}$: 46 s : 6 RSD% : 13
Ba	41	$\bar{X}$: 50,6 s : 8 RSD% : 15,8
Cu	38	$\bar{X}$: 44,8 s : 9,4 RSD% : 21
Sr	78	$\bar{X}$: 73,2 s : 5 RSD% : 6,8
Pb	39	$\bar{X}$: 35 s : 5 RSD% : 6,8
La	36	$\bar{X}$: 35 s : 6 RSD% : 14
Ce	39	$\bar{X}$: 32 s : 6 RSD% : 18,8
Co	35	$\bar{X}$: 44,8 s : 9,3 RSD% : 20
Ti	50	$\bar{X}$: 44 s : 6,8 RSD% : 15,4

The possibility to analyse rare earths at ultra-trace level (less than 10 $\mu g \cdot g^{-1}$ in the solid samples) was also investigated. At this level, there is also a good agreement between LA-ICP-MS and solution analyses (Table 8).

The elements which can be determined in LA-ICP-MS are the same as in the conventional nebulisation ICP-MS but memory effects are different. In ICP-MS these effects occur on the glassware and cones but in LA-ICP-MS they mostly occur in the ablation chamber and the transfer tube. In conventional ICP-MS, there is always an exchange between the fresh aerosol and solution droplets present on the walls of the spray chamber but which gives rise to memory effects. However in LA-ICP-MS no mechanisms exist for similar exchange and once particles are lost from the dry aerosol to the walls they remain there.

In addition, LA-ICP-MS does not involve any water, and therefore minimizes the problems linked to oxide formation which are mainly due to solvent water. This

Table 4. Results for Titanium (in LA-ICP-MS and ICP-MS the results are obtained in semi-quantitative mode)

Glasses	Titanium ($\mu g \cdot g^{-1}$)		
Reference	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)
1	299	290	310
2	180	150	180
3	210	264	240
4	180	170	184
5	269	200	310
6	150	120	150
7	90	85	105
8	120	100	115
9	305	210	280
10	210	220	210

Table 5. Results for manganese and zirconium (in LA-ICP-MS and ICP-MS the results are obtained in semi-quantitative mode)

Glasses	Manganese ($\mu g \cdot g^{-1}$)			Zirconium ($\mu g \cdot g^{-1}$)		
Reference	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)
1	70	55	64	52	43	50
2	70	57	70	<30	23	18
3	78	90	83	—	56	53
4	2100	1800	2000	—	330	350
5	109	84	104	—	60	70
6	31	28	39	81	81	86
7	54	40	44	—	45	37
8	<39	18	26	—	70	40
9	62	57	62	—	50	61
10	39	32	37	—	40	25

is a distinct advantage for the determination of the heavy rare earth elements which are hindered by isobaric interferences from oxides of the light rare earths [5] and for the determination of elements like iron (ArO^+ interference) at low level. The spectra II and III show the background reduction (factor 100) on mass 56 for nitric acid blank (1%) in conventional nebulisation ICP-MS and the signal for a dry plasma in LA-ICP-MS (Figs. 3 and 4).

Table 6. Results for barium and lead (in LA-ICP-MS and ICP-MS the results are obtained in semi-quantitative mode)

Glasses	Barium ($\mu g \cdot g^{-1}$)			Lead ($\mu g \cdot g^{-1}$)		
Reference	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)
1	—	65	65	14	7	7
2	—	50	50	14	8	8
3	—	80	65	—	4	4
4	—	64	63	—	16	13
5	—	60	65	—	14	16
6	—	13	12	—	2	2
7	—	20	22	—	5	4
8	—	17	19	—	6	7
9	—	25	24	—	6	3
10	—	103	107	—	5	4

Table 7. Results for strontium and copper (in LA-ICP-MS and ICP-MS the results are obtained in semi-quantitative mode)

Glasses	Strontium ($\mu g \cdot g^{-1}$)			Copper ($\mu g \cdot g^{-1}$)		
Reference	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)	Indicative	LA-ICP-MS	Mineralisation (ICP-MS)
1	68	82	92	—	5	4
2	34	34	50	—	2,5	2,5
3	—	115	100	—	6	5
4	—	22	20	—	10	11
5	—	40	60	—	2,5	2
6	—	37	48	—	6,4	4
7	—	120	100	—	7	3
8	—	93	100	—	3	2
9	—	30	33	—	6	4
10	—	40	44	—	9	4

Conclusion

The decomposition of a glass sample into a solution suitable for conventional ICP-MS analyses is time consuming (several hours), sometimes not successful. In addition, losses of elements and contamination problems may occur for many elements. The validity of the described technique, which allows the direct analysis of solid samples without any preparation, is demonstrated by the agreement with more conventional, but time consuming methods. The semi-quantitative results obtained by this technique are excellent. The deviations from the indicative values range from a few % up to 20% for all the elements irrespective of their concentrations.

Table 8. Results for lanthanum, cerium and yttrium (in LA-ICP-MS and ICP-MS the results are obtained in semi-quantitative mode)

Glass	Lanthanum ($\mu g \cdot g^{-1}$)		Cerium ($\mu g \cdot g^{-1}$)		Yttrium ($\mu g \cdot g^{-1}$)	
Reference	LA-ICP-MS	Mineralisation (ICP-MS)	LA-ICP-MS	Mineralisation (ICP-MS)	LA-ICP-MS	Mineralisation (ICP-MS)
1	3	3	4	4	3	3
2	2,4	3	4	4	3	3
3	3	2	5	3	4	3
4	3	4	6	9	5	6
5	3	5	6	8	3	3
6	3	3	4	4	3	4
7	2	2	2,5	3	2	2
8	2	2	3	4	2	2
9	2	2,5	3	4	2	2
10	7	5	8	6	11	9

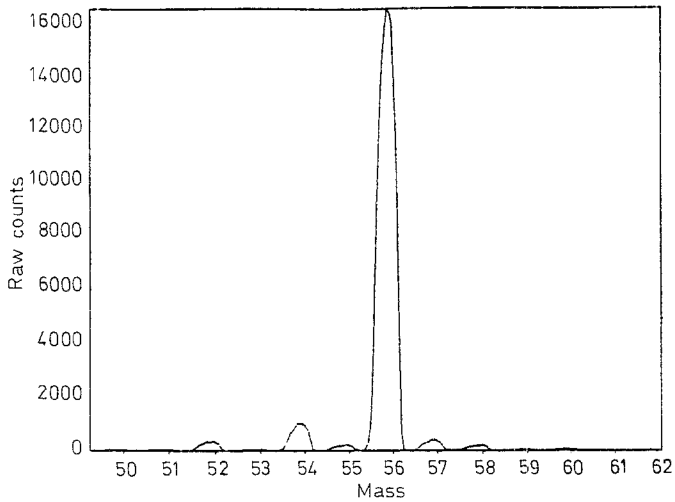

Fig. 4. Signal for a nitric acid blank (1%)

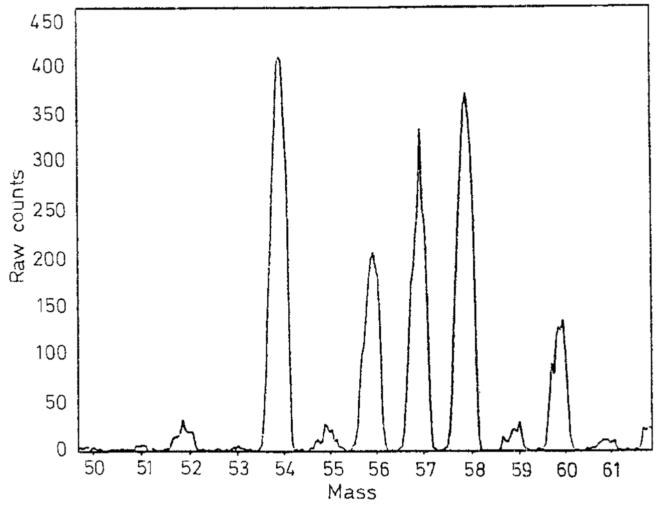

Fig. 5. Signal for a dry plasma

From a practical point of view, LA-ICP-MS compares somewhat to X-ray fluorescence spectrometry (XRF), an other purely instrumental technique. Although XRF is a very precise and accurate technique, its sensitivity is limited, and only major and a few minor elements can be determined. In contrast, LA-ICP-MS has very low detection limits and much better spatial resolution. Both techniques may prove complementary for the direct analysis of glass samples.

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