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# Nanosecond laser ablation tandem inductively coupled plasma mass and optical emission spectrometry for micro-chemical elemental analysis†

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A novel experimental system was designed for micro-chemical elemental analysis using a laser ablation technique tandem to both mass and optical emission spectrometry. One new excimer gas laser of 193 nanometer wavelength was constructed to replace the COMPexPro 102 laser unit in the RESolution M50 laser ablation system without changing the ablation cell. The ablated mass (aerosol) was introduced into the inductively coupled plasma mass spectrometer, *i.e.* Agilent 7500, where optical emission spectrometry was performed simultaneously using an Ocean Optics fiber optic spectrometer. The fiber optic spectrometer consists of six channels, which can detect the optical emission lines from plasma and cover wavelengths from 190 nm to 800 nm. Standard reference materials were measured for demonstrating the elemental analytical method. The constant LA-ICP-MS transient signals, acceptable concentration determinations of MPI DING glass ATHO or T1 samples and negligible differences of elemental fractionation due to replacement of the laser source in RESolution M-50 suggest that our newly constructed excimer gas laser can satisfy LA-ICP-MS micro-chemical analysis. Furthermore, the laser ablated particle resultant inductively coupled plasma optical emission lines can be identified, and the quite good linear correlation of signals in various emission lines of the same element analysed suggests that the wavelength resolution necessary for quantitative elemental analysis by LA-ICP-OES can be achievable using a fiber optic spectrometer. Finally, based on sharing the same inductively coupled plasma configuration in our new LA-ICP-MS & OES system, the linear correlation between signals of LA-ICP-MS and LA-ICP-OES for the same elements can be recognized. The calibration curves for optical emission lines of element manganese, and the coefficient ratios around 0.999, suggest that the novel method of LA-ICP-MS & OES might be a feasible option for micro-chemical elemental analysis through synchronously detecting the stoichiometric composition in the laser ablated mass resultant inductively coupled plasma.

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## Introduction

Laser ablation (LA) of solid samples followed by transportation of atomic vapors and aerosol particles to a measuring device

has been used for *in situ* micro-chemical analysis over the last two decades.<sup>1</sup> LA micro-chemical analysis can work with a mass or optical spectrometer with inductively coupled plasma as the analytical excitation source. The laser ablated mass can be carried by inert gas to the ICP excitation source, where the resulting spectra from ICP-MS or ICP-OES can be used to show the elemental quantification information in the sample. As a result, the tandem LA-ICP-MS is one of the effective multi-elemental analysis techniques for solid samples, and LA-ICP-OES is another promising technique that in some circumstances can satisfy the requirement of higher precision.<sup>2</sup>

The pioneering work<sup>3</sup> reported one instrumentation design assembling both the ICP-MS and ICP-OES techniques for simultaneous determination of major and trace elements. Subsequent studies<sup>4,5</sup> also explored the plausibility of sharing the same ICP for two distinctive detection systems. Recently, Yujia Deng *et al.* (2017) reported a simultaneous elemental

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analysis system by sharing one ICP for ICP-MS and ICP-OES. These studies applied two ICP detecting approaches, *i.e.* mass spectrometry and optical emission spectrometry. An optical fiber was used to transmit light sources resulting from optical emission in the ICP and one spectrometer was used to detect these light signals quantitatively thereafter. Although the signals resulting from element Mg in the ICP detected by the two systems correlate well,<sup>6</sup> more improvements are needed before presenting one robust simultaneous elemental analysis approach. Considering the spectral interference due to more than 50 000 ICP-OES spectral lines documented and the limited wavelength range of only about 600 nanometers covered in general, as well as the transmission loss of light sources due to the optical fiber connected between the ICP and the CCD spectrometer, it is urgent to optimize these two ICP synchronous detection approaches.

In this work, we upgraded the optical emission detection hardware system design by optimizations of both CCD spectrometer and light source sampling positions. In the meantime, we constructed one new excimer gas laser of 193 nm wavelength and replaced the COMPexPro 102 laser unit built in the original RESOLUTION M50 laser ablation system without changing the ablation cell any more. It is shown that the multi-channel optical fiber spectrometer can satisfy the requirements of both full spectrum direct reading and high enough wavelength resolution power. Furthermore, the modified laser ablation system due to replacement of the excimer laser source can be successfully tandem to both the ICP-MS and the ICP-OES. SRM 610 and MPI DING glass standard materials were laser ablated and measured synchronously by ICP-MS and ICP-OES. It is suggested that the new modified LA-ICP-MS & OES system can be used for *in situ* multi-elemental analysis in solid samples.

## Experimental

### ICP-MS & OES configuration

The schematic diagram of the experimental setup is shown in Fig. 1, in which one laser ablation unit and another spectrometry detection unit are included. An excimer gas laser (labelled PLD 30 and developed by Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, China) was used as the source for 193 nm (pulse energy can vary from 130 mJ to 212 mJ and 300 mJ under the conditions of high voltage of 28.5 kV, 30.5 kV and 32 kV, pulse width 20 ns, and beam size approx.  $22 \times 8 \text{ mm}^2$ ) to replace the original excimer gas laser COMPexPro 102 (manufactured by Coherent Co., USA) in the RESOLUTION M50 laser ablation system, while other optical configurations, including the laser ablation cell, the squid smoothing device and the X-Y stage, were unchanged.<sup>7</sup> This experimental setup allows the irradiation of the sample as less changed due to the replacement of the laser as possible. There are two parallel parts for the spectrometry detection unit. The mass spectrometry part is routine, and one optical spectrometer is tandem to a conventional ICP torch chamber by optical fiber connection, and thus to build the ICP-OES setup.

The modified RESOLUTION M-50 laser ablation system was tandem to one Agilent 7500 ICP-MS. The ICP-MS signal was detected by the 7500 ICP-MS system and the ICP-OES signal was synchronously detected by an Ocean Optics MX2500+ using a six-channel optical spectrometer (manufactured by Ocean Optics, USA) which can detect simultaneously the optical emission lines from inductively coupled plasma covering wavelengths from 190 nm to 800 nm. A radiation homogenizer unit positioned serves to facilitate beam delivery in the modified LA system, and a flat-top beam was shaped and imaged onto sample surfaces giving fluences up to  $14.5 \text{ J cm}^{-2}$  instead

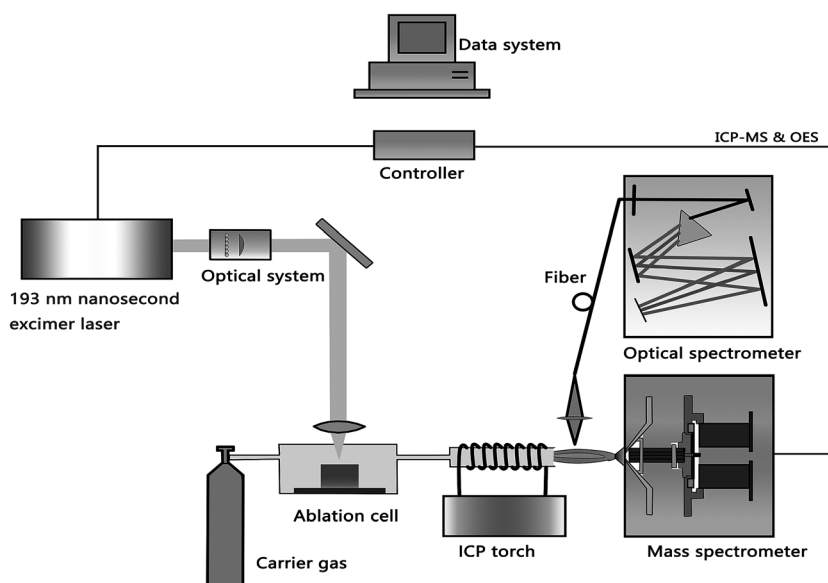


Fig. 1 Schematic diagram of LA-ICP-MS & OES elemental analysis by synchronous spectra detection devices.

of the original  $3.7 \text{ J cm}^{-2}$ . The performance of the modified RESOLUTION M-50 laser ablation system was evaluated through routine LA-ICP-MS analysis which shows that there exist negligible differences due to replacement of the excimer gas laser source and our newly constructed excimer gas laser can satisfy LA-ICP-MS micro-chemical analysis (see details in the ESI†).

The spot size and repetition rate of laser parameters were varied in order to evaluate the performance of LA-ICP-MS & OES based on the modified LA system. Besides line-scan laser ablation mode, single-site mode analysis was also carried out to evaluate the performance of the newly constructed modified RESOLUTION M50 laser ablation system. A laser ablation time of 240 seconds following the 20 s blank time and followed by a 30 s ablation cell wash time for every LA-ICP-MS & OES measurement was configured. A summary of the operating conditions used for laser ablation, ICP-MS and ICP-OES is given in Table 1. The performance evaluation for elemental concentration determination of MPI DING glass samples was carried out and NIST 610 served as an external calibration standard.

## Samples

The NIST SRM 610 and MPI DING glass samples (coded T1 and ATHO respectively) were selected for all measurements of LA-

ICP MS & OES. The reference values for all standards were taken from the literature.<sup>8</sup> Diluted solutions of element Mn (purchased from National Standard Material in China) in different concentrations were prepared for ICP-OES standard calibration curve measurements.

## Results and discussion

Although both the mass spectrometry and optical emission spectrometry techniques can independently perform elemental analysis on the basis of a stoichiometric representation of the ablated aerosol, it might be impossible to simultaneously determine the elemental concentration before the transient signals and standard calibration curves of the new LA-ICP-MS & OES tandem system are investigated in detail.

### LA-ICP-MS & OES signal

The transient time signals of three isotopes detected ranging from low to high mass ( $^{66}\text{Zn}$ ,  $^{88}\text{Sr}$ , and  $^{238}\text{U}$ ) using the PLD 30 excimer gas laser based LA-ICP-MS are displayed in Fig. S1(a-c) (see the ESI†), and the line-scan mode results in an approximately constant signal during the whole four minute ablation process.

ICP-OES will probably never become as sensitive as ICP-MS. Through sharing the same ICP excitation source, previous

Table 1 Summary of the operating conditions used for LA-ICP-MS & OES measurements

Parameters	ArF excimer gas laser					
Type (developer or manufacturer)	PLD 30 (Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, China)			COMPexPro 102 (Coherent Co., USA)		
Wavelength (nm)	193			193		
Laser high voltage (kV)	28.5, 30.5, and 32					
Pulse energy (mJ)	130, 212, and 300			200 (maximum)		
Pulse width (nanosecond)	20			20		
Repetition rate (Hz)	5, 8, 10, and 15			5, 8, 10, and 15		
Ablation cell gas	He			He		
Spot size ( $\mu\text{m}$ )	33, 82, 155, and 285			33, 45, 82, and 155		
Energy density ( $\text{J cm}^{-2}$ )	14.5			3.7		
Ablation mode	Single-site, line-scan ( $8 \mu\text{m s}^{-1}$ )			Single-site, line-scan ( $8 \mu\text{m s}^{-1}$ )		
Ablation duration (second)	240 and 40			240		
ICP-MS conditions						
Carrier gas flow ( $\text{L min}^{-1}$ )	0.85 (Ar)					
Plasma gas flow ( $\text{L min}^{-1}$ )	15 (Ar)					
RF power (W)	1350					
Integration time (ms)	20					
Isotopes measured	$^{23}\text{Na}$ , $^{24}\text{Mg}$ , $^{27}\text{Al}$ , $^{29}\text{Si}$ , $^{31}\text{P}$ , $^{39}\text{K}$ , $^{43}\text{Ca}$ , $^{45}\text{Sc}$ , $^{47}\text{Ti}$ , $^{51}\text{V}$ , $^{53}\text{Cr}$ , $^{55}\text{Mn}$ , $^{57}\text{Fe}$ , $^{75}\text{As}$ , $^{85}\text{Rb}$ , $^{88}\text{Sr}$ , $^{90}\text{Zr}$ , $^{208}\text{Pb}$ , $^{232}\text{Th}$ , and $^{238}\text{U}$					
ICP-OES conditions						
Wavelength range	190–800 nm					
Channels	A	B	C	D	E	F
Wavelength ranges (nm)	190–250	230–330	320–410	400–525	510–620	610–795
Integration time (ms)	600	600	600	300	300	300
Wavelength resolution (nm)	0.1					
Emission line, $\lambda$ (nm)	588.896 (Na), 589.486 (Na), 393.346 (Ca), 396.828 (Ca), 288.055 (Si), 260.355 (Mn), 259.185 (Mn), 257.457 (Mn), and 251.678 (Si)					

studies have reported the possibility and practicality of ICP-OES tandem to ICP-MS.<sup>3–6</sup> However, as the routine laser ablation process only generates limited mass of samples, *e.g.* less than micrograms or even nanograms, it is critical to select one sensitive enough optical emission spectrometer before we can simultaneously measure laser generated aerosol resultant LA-ICP-OES as well as LA-ICP-MS. Simultaneous LA-ICP-OES signals are measured using a fiber optic spectrometer Ocean Optics MX2500+ (Fig. 1) under the conditions given in Table 1. The spot size and repetition rate of laser parameters in the PLD 30 excimer gas laser varied independently. As a result, the aerosols transported into the ICP may vary, and thus the compositions in the laser ablated mass resultant ICP varied. Fig. 2a shows the detected optical emission lines of major elements Ca, Si, and Na for sample NIST 610. The quite good linear correlation between optical emission lines in the same element, *e.g.* correlation coefficient of 0.9999 for two emission lines (251.678 nm and 288.055 nm) in element Si (Fig. 2b) and 0.9968 for two emission lines (393.346 nm and 396.828 nm) in element Ca (Fig. 2c), suggests that sensitive enough optical emission lines from laser ablation generated aerosol resultant ICP can be detected in one quantitative way. In the case of less sensitive lines, the spectral interference might be serious and the correlation coefficient for two emission lines (588.896 nm and 589.486 nm) in element Na reduced to 0.9866 (Fig. 2d). As a result, appropriate selections of optical emission lines for certain elements in our new LA-ICP-OES configuration should be determined before any possible quantitative elemental analysis.

It also makes it possible to measure the dependence of LA-ICP-MS & OES signals on the ablated mass of samples and check if the alteration of the stoichiometric compositions within the laser-generated aerosol can be quantified by LA tandem ICP-MS and ICP-OES techniques. The effects of spot size and repetition rate of laser parameters in the PLD 30 excimer gas laser (Table 1) on LA-ICP-MS signals of major elements Na, Mg, Al, Si, and Ca are given in Fig. 3a, and those on LA-ICP-OES signals of major elements Si and Na are given in Fig. 3b. LA-ICP-MS and LA-ICP-OES signals are calculated through averaging transient signals during 240 seconds of laser ablation, and normalized by each corresponding maximum value. It can be seen that there is an increasing trend in the LA-ICP-MS signal as the spot size or repetition rate increases independently, and the maxima signals of five elements are all measured under the conditions of a repetition rate of 10 Hz and a spot size of 285  $\mu\text{m}$ . Furthermore, the 10 Hz repetition rate leads to approximately double the intensity of the LA-ICP-MS signal in comparison with the 5 Hz repetition rate. As the time-dependent removal (laser ablation) of mass from a sample is determined by the combined instrumental parameters of wavelength, energy, pulse duration, the sample itself, repetition rate, ablation mode<sup>9</sup> *etc.*, the increase in signals could be due to an increase in ablation as a result of increasing the repetition rate or spot size.<sup>10,11</sup> For example, the normalized LA-ICP-MS signal intensity of the <sup>29</sup>Si isotope changes from 0.53 to 0.66 and 1.0 due to varying the repetition rate from 5 Hz to 8 Hz and 10 Hz under the same spot size of 285  $\mu\text{m}$ . Considering the line-

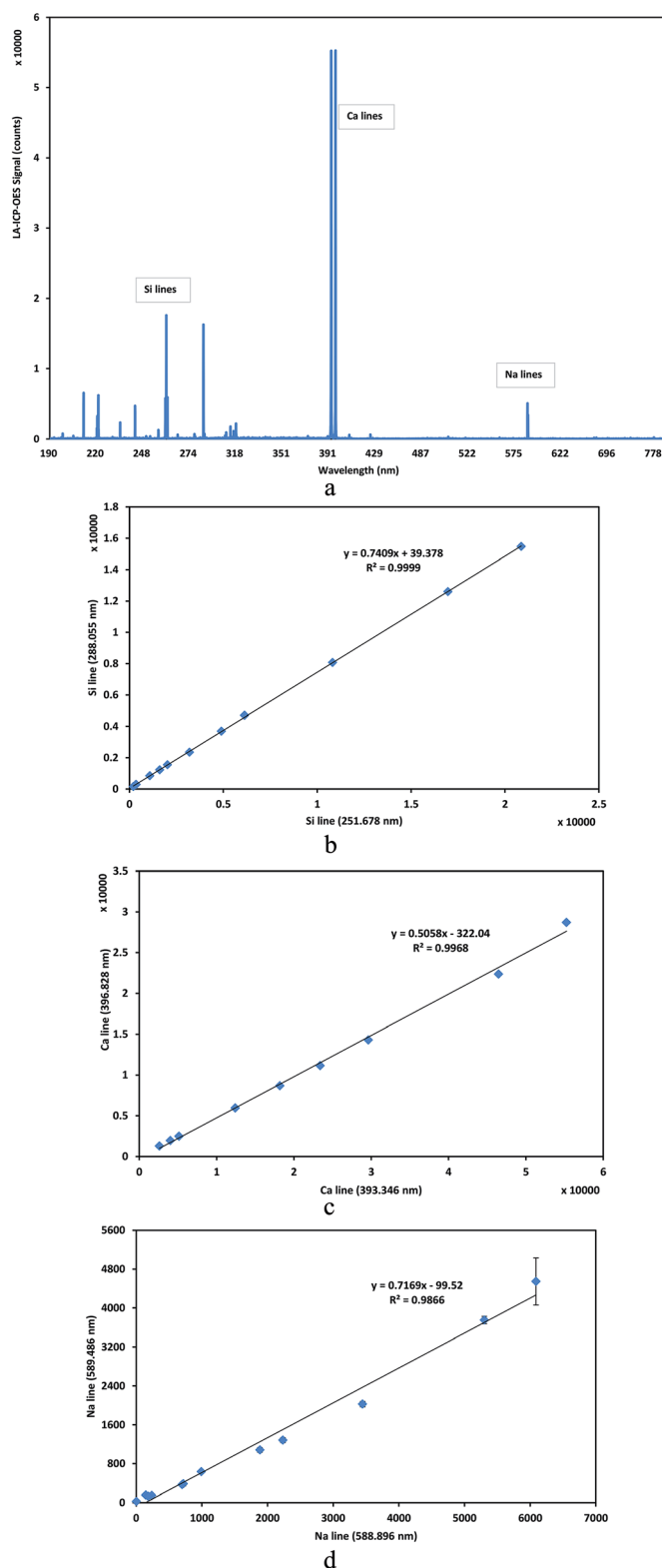


Fig. 2 The simultaneous LA-ICP-OES measurements for sample NIST 610 under the same conditions as in Fig. S1.† Detectable optical emission lines (a). Each data point in (b–d) is calculated by averaging the three ICP-OES signals sampled during the synchronous 240 second laser ablation time. Each different ablated mass of samples in (b–d) was due to variations in parameters of laser PLD 30, *e.g.* repetition rate, laser pulse fluence or energy (Table 1).

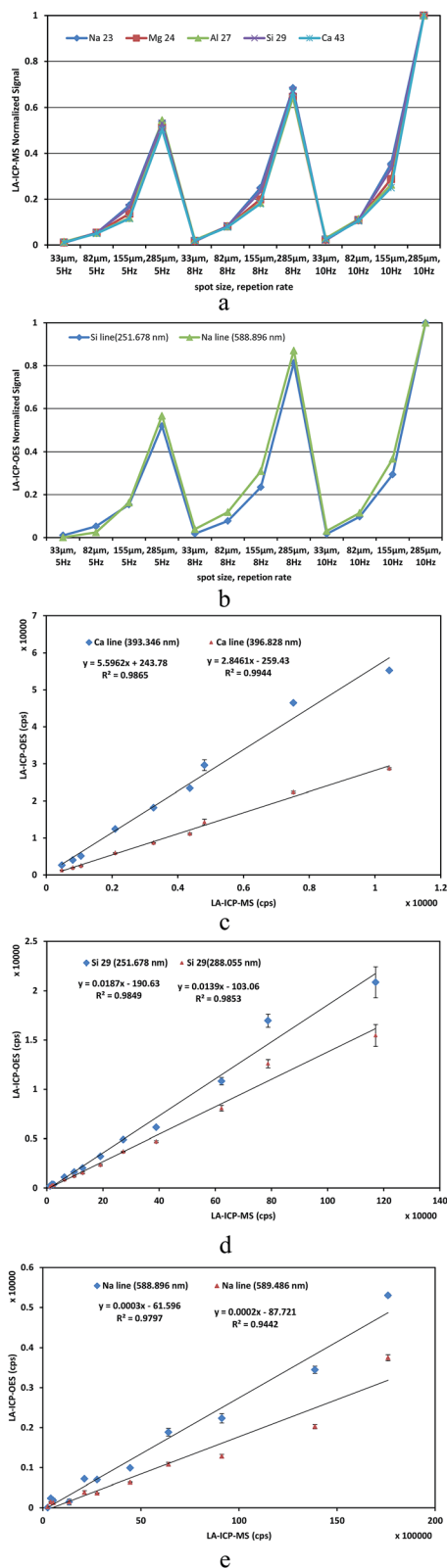


Fig. 3 ICP-MS signal intensity (a) of isotopes ( $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ , and  $^{43}\text{Ca}$ ) and ICP-OES signal intensity (b) of Si and Na emission lines under the conditions of varying spot size and repetition rate in laser parameters of PLD 30, normalized to the corresponding maximum intensity. And each data point in (c–e) is calculated by averaging the ICP-MS and ICP-OES signals sampled during the synchronous 240 second laser ablation time. Each different ablated mass of samples in

scan speed of  $8 \mu\text{m s}^{-1}$ , the maximum spot size of  $285 \mu\text{m}$  and the approximate ablation depth rate of  $0.11 \mu\text{m}$  per pulse,<sup>12</sup> there are around 356 laser pulses, or a depth of *ca.*  $39.2 \mu\text{m}$  at a particular location at the repetition rate of 10 Hz. As a result, the aspect ratios determined by crater depth/diameter are all well below 1 for all the spot sizes at independently varied repetition rates.<sup>11</sup> Therefore, the increase of LA-ICP-MS signals might be decided mainly by repetition rates.<sup>13,14</sup> As expected, the variations of LA-ICP-OES signals (Fig. 3b) display the same pattern as those of LA-ICP-MS signals (Fig. 3a) due to varied laser parameters. For example, the normalized LA-ICP-OES signal intensity of  $^{29}\text{Si}$  changes from 0.52 to 0.81 and 1.0 due to varying the repetition rate from 5 Hz to 8 Hz and 10 Hz under the same spot size of  $285 \mu\text{m}$ . The synchronous variations of both LA-ICP-MS and LA-ICP-OES (Fig. 3a and b) might evidence the practicability of simultaneous elemental analysis by the LA-ICP-MS & OES approach.

The inter-comparisons of ICP-MS and ICP-OES signals for elements Si, Ca and Na are shown in Fig. 3(c–e) respectively. The linear correlation of the ICP-OES signal with the corresponding ICP-MS signal, for example, the coefficients of 0.9944 for Ca ( $396.828 \text{ nm}$  emission line) (Fig. 3c) and 0.9853 for Si ( $288.055 \text{ nm}$  emission line) (Fig. 3d), might lend evidence to the internal standard selection of element Ca or Si for the ICP-MS based elemental analysis approach. Quantification of LA-ICP-OES emission lines for the major elements shown in this work might be one good addition to the elemental analysis work if major element quantification by the LA-ICP-MS approach shows poor quality.

### Performance of the new LA-ICP-MS & OES

The performance of the modified laser ablation unit based LA-ICP-MS was examined under the following laser parameters: a repetition rate of 8 Hz, a spot size of  $82 \mu\text{m}$  and a fluence of  $14.5 \text{ J cm}^{-2}$ . Concentrations of 38 elements in two MPI DING glass samples (coded ATHO and T1) were determined using NIST SRM 610 as an external reference material and Ca or Si as an internal standard. Data reduction was performed using ICPMSDataCal software (China University of Geosciences). This software displays the time resolved spectrum for each analysed mass and allows the selection of the most appropriate part of the spectrum for calculating elemental concentrations. An internal standard is used to correct the variations in the absolute amount of materials ablated during each run. For this study, internal standardization was performed using Ca and Si.<sup>15</sup> The 38 element analysis results were compared with reference values.<sup>8</sup> Fig. 4a and b show the relative deviations of the determined concentrations in the two geological reference glasses from the reference values. The calculated deviations from the reference values were within  $\pm 10\%$  except in the case of elements Sc, V, Cr, Ni, Co, Cs, Ge, Zn and Ba in sample ATHO, and Cr, Ni, Ga, As, Ge, La and Pb in sample T1. It can be seen

(c–e) was due to variations in parameters of laser PLD 30, e.g. repetition rate, laser pulse fluence or energy (Table 1). The error bars in (c–e) show the standard deviation after three repeat measurements.

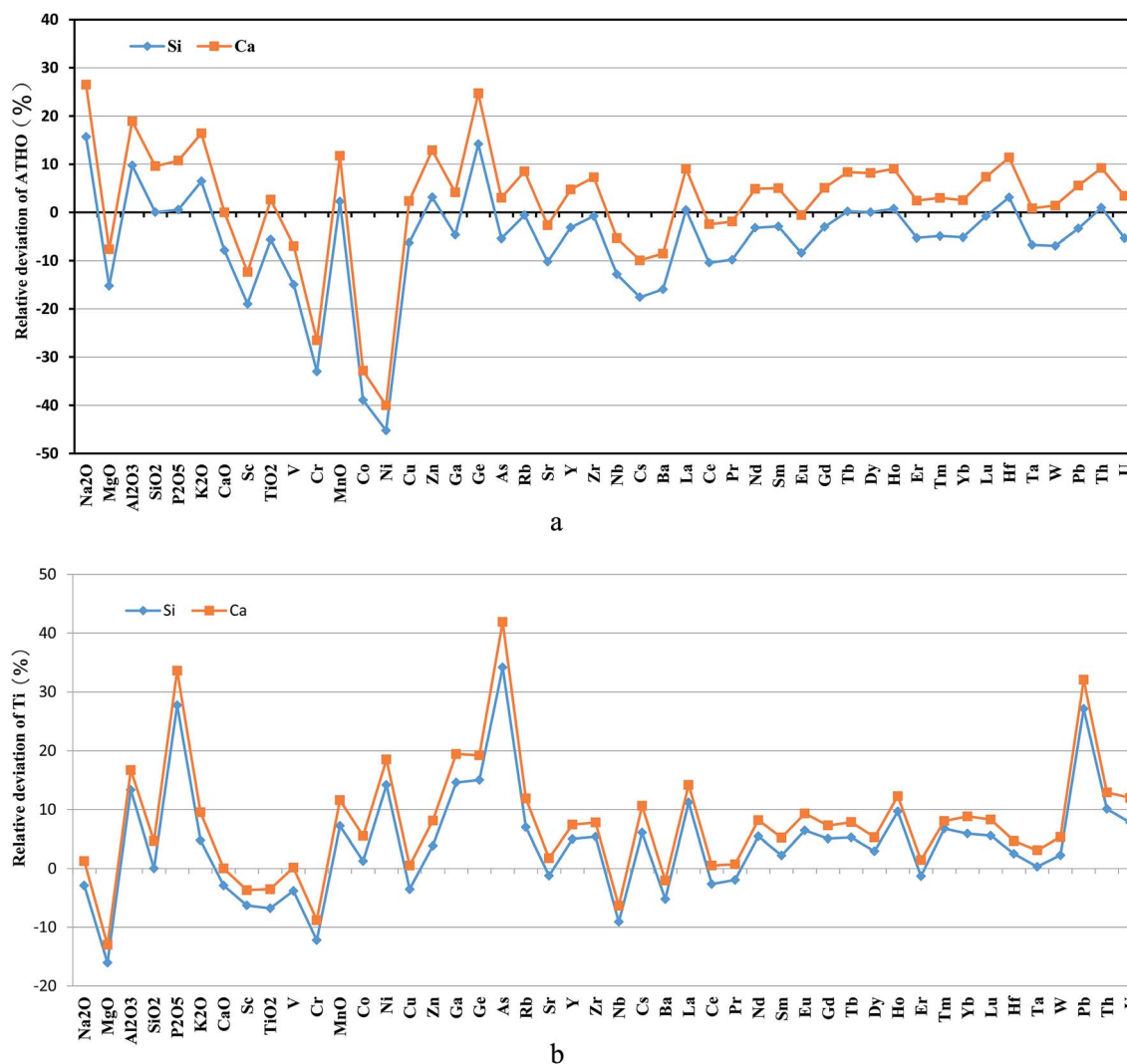


Fig. 4 LA-ICP-MS analysis of 38 element concentration determination for MPI DING glass sample ATHO (a) and T1 (b) using the internal standard of Ca and Si respectively. The relative deviation in percentage was calculated by the ratio of the difference between the determined concentration and the corresponding reference value to the reference value.

that there exist differences in the concentration determination of MPI DING glass samples if the selection of the internal standard varies, *e.g.* Ca or Si. Fewer deviations from the reference values for both ATHO and T1 glass samples can be recognized when the combined selection of the external standard of NIST 610 and the internal standard of Si is made. Although this difference in the accuracy of elemental determination resulting from internal standard selection cannot be evidenced by the correlation of LA-ICP-MS signals and LA-ICP-OES signals in elements Si and Ca (Fig. 3c and d), the simultaneous elemental determination by the LA-ICP-OES approach might open another way to reduce the non-spectroscopic interference resultant elemental fractionation in the LA-ICP-MS approach, *e.g.* the poor quality for major element determination shown in Fig. 4a and b, *e.g.* elements of Ca, Si, Na, Cr, *etc.*

It is a pity that we cannot detect optical emission lines of trace elements, like Sc, V, Cr, Ni, Co, Cs, Ge, Zn and Ba in sample ATHO, and Cr, Ni, Ga, As, Ge, La, and Pb in sample T1,

for which the concentration determination using our new LA-ICP-MS displays poor quality. It seems that our LA-ICP-OES might be appropriate for ppm or larger scale concentration determination.

The significance of standard calibration in both ICP-MS and ICP-OES has been evidenced. In our LA-ICP-MS & OES system setup, the good linear correlation between ICP-MS and ICP-OES signals (Fig. 3c-e) and the satisfactory linear inter-correlation between two ICP-OES lines (Fig. 2b-d) in selected elements might suggest that this ICP-OES setup can be used for stoichiometric application in elemental analysis.

We turned the sample introduction to a routine nebulizer sample introduction system, and diluted solutions of manganese of 1 ppm and 20 ppm were introduced into the ICP. The ICP optical emission lines of element manganese at 257.457 nm, 259.185 nm and 260.355 nm were recognized (Fig. 5a). The corresponding standard calibration curves are

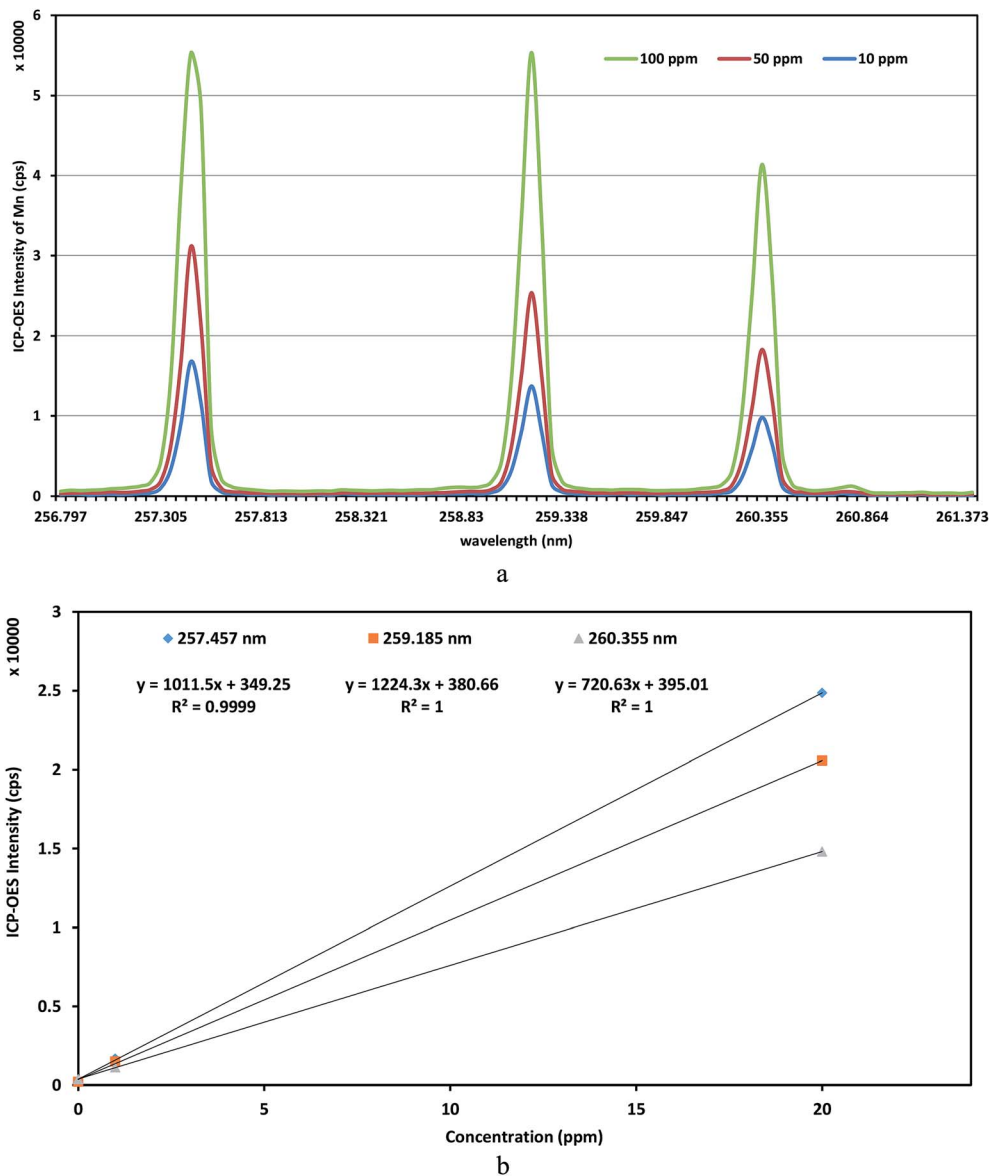


Fig. 5 ICP-OES signals from diluted solutions of manganese at the given concentrations (a), and the standard calibration curves for each optical emission line of 257.457 nm, 259.185 nm and 260.355 nm (b); the standard solutions of manganese were diluted to 1 ppm and 20 ppm respectively, including one blank concentration.

given in Fig. 5b, which show quite good linear response ranging from 1 ppm to 20 ppm.

## Conclusions

A modified LA-ICP-MS & OES system setup was proposed in this work based on a RESOLUTION M50 laser ablation system and Agilent 7500 ICP-MS. The constant LA-ICP-MS transient signals, acceptable concentration determinations of MPI DING glass ATHO or T1 samples and negligible differences of elemental fractionation due to replacement of the laser source in RESOLUTION M-50 suggest that our newly constructed excimer gas laser can satisfy LA-ICP-MS micro-chemical analysis.

The laser ablated particle resultant inductively coupled plasma optical emission lines can be identified. The quite good linear correlation of signals in various emission lines of the same element analysed suggests that the wavelength resolution necessary for quantitative elemental analysis by LA-ICP-OES can be achievable using a fiber optic spectrometer.

Based on sharing the same inductively coupled plasma configuration in our new LA-ICP-MS & OES system, the effects of spot size and repetition rate of laser parameters in our newly constructed PLD 30 excimer gas laser on both LA-ICP-MS and LA-ICP-OES signals exhibit the same pattern. Furthermore, the linear correlation between signals of LA-ICP-MS and LA-ICP-OES for the same elements can be recognized. Finally, standard calibration curves obtained by ICP-OES through routine

nebulizer sample introduction of diluted solutions of manganese show quite good linear response. It is thus suggested that the novel method of LA-ICP-MS & OES might be a feasible option for micro-chemical elemental analysis through simultaneously detecting the stoichiometric composition in the laser ablated mass resultant inductively coupled plasma.

## Conflicts of interest

There are no conflicts to declare.

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