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Short communication

A simple laser ablation ICPMS method for the determination of trace metals in a resin gel

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ABSTRACT

Trace metal analysis of DGT gels using laser ablation inductively coupled plasma (LA-ICP-MS) has traditionally been carried out by ablating single spots along a line to provide high resolution data on trace metal distributions on a resin gel. This work compares the performance of two different LA-ICPMS systems, one at Lancaster University, UK and another at VUB, Belgium, in terms of instrument sensitivity and limit of detection in the analysis of trace metals (Co, Ni, Cu, Zn, Cd, and Pb) bound by a DGT resin gel using SPR-IDA resin. No defocusing of the laser beam was necessary to prevent burning through the resin gel and the internal standardization became very simple by using ^{13}C, naturally present in the resin-gel, instead of impregnating a back-up layer with ^{115}In.

Furthermore, this work also explores the option of analysing the spatial distribution of resin bound trace metals by means of ablating a continuous line between two points and considers the advantages of using this approach.

The work found that the LODs assessed on blank samples for Cu and Pb are similar for both LA-ICPMS systems, while for Co, Ni and Zn they are lower for the one at VUB and for Cd for the other one at Lancaster. The work found that the laser ablation systems at the two laboratories allowed more precise control over laser power and spot size than previously reported. For the line scan, the optimum scan parameters were determined as: scan speed of 50 μm s^{-1}, output energy of 40% and repetition rate of 30 Hz. An acquisition time of 25 ms, resulted in a much lower resolution (10 μm) compared to the spot ablation (a crater size of 100 μm and also some space between craters) and a better sensitivity. The LODs using the line scan were found to be lower than those obtained by the spot ablation. However, for some of the metals the difference is rather small. This work suggests that the time and gas consumption achieved by using the line scan is about 30% lower than for the traditional spot scan.

1. Introduction

The study of bioavailable trace elements in marine systems is an important topic in environmental sciences because it can help to explain limitation of primary productivity in open ocean areas such as the Antarctic Ocean [1] or the change in diversity of bacterial communities in marine sediments [2]. Diffusive gradients in thin (DGT) films has been used to assess trace metal concentrations and bioavailability in a variety of natural media, such as aquatic environments [3], soils [4] and sediments [5–7]. DGT works by incorporating a chelating resin, such as Chelex 100, into a layer of polyacrylamide hydrogel which binds metal from solution. When deployed in a water column, the standard DGT probe is shaped like a piston and the resin used to bind the metal is fixed within a disc of hydrogel [8]. To assess the concentrations accumulated by the resin gel in a DGT piston device, the entire resin gel disc is eluted with 1 M nitric acid, after which the eluate is analysed using inductively coupled plasma mass spectrometry (ICPMS). A standard DGT sediment probe is rectangular, with an elongated *z*-axis, where the actual surface of the probe is normally 18 mm × 150 mm. To assess the metal bound by the resin in the sediment probe, the resin gel is first sectioned into small slices (for example: 18 mm × 5–10 mm size), after which each slice is eluted with 1 mol L^{-1} nitric acid, which is then analysed. This allows for the determination of metal profiles in relatively high resolution across the depth profile, both in situ and in laboratory conditions, with minimal perturbation to the sediment being measured.

Through its simplicity and versatility DGT provides a number of advantages over other methods of determining trace metal concentrations and bioavailability in aquatic systems and is therefore

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a highly useful tool for biogeochemists. However, there are still plenty of opportunities to extend its utilization and to improve its performance. For example, the elution of metal from the resin gel effectively destroys the sample and cannot be used for any other purpose afterwards. A second restriction is the practical limitations to achieving extremely high vertical resolution that can be obtained with the slicing technique: a vertical resolution of less than a few mm is very difficult to achieve in practice and in some cases this is not sufficient to understanding sediment microstructure [9]. The use of Chelex-100 resin further complicates the issue as Chelex beads are ~100 μm in diameter which further restricts the spatial resolution that can be achieved [10].

A solution to overcome these limitations is (1) the use of highly specific, high resolution beam techniques that allow multiple analyses on a single DGT resin, while maintaining relatively high resolution and (2) the use of a binding resin where the beads are smaller than those of Chelex-100. Proton-induced X-ray emission (PIXE) was the first high resolution sampling method utilizing suspended particulate reagent-imidodiacetate (SPR-IDA) resin [10], but this is a complicated method [11]. The latter authors demonstrated the applicability of SPR-IDA that has a bead size of only 0.2 μm, as a substitute for Chelex in binding trace metals. Warnken et al. [12] used laser ablation ICPMS (LA-ICPMS) to analyse trace metals (Co, Ni, Cu, Zn, Cd, and Pb) bound onto resin-gels at a spatial resolution of 100 μm.

The technique presented by Warnken et al. [12] is less complicated than PIXE, however, there is still room for improvement. First, his technique still warrants the use of a backing layer containing a number of internal standards (such as, indium scandium, rhodium and others) to correct for fluctuations of the laser and the ICPMS. There are a number of disadvantages to this approach: (1) there is the possibility of other metals contaminating the In-loaded resin gel during its preparation, which would result in higher blank levels; (2) in sediments/soils where there is a high concentration of cadmium (or localised microfeatures with high concentrations of Cd), there is the possibility of polyatomic interference from $^{114}Cd^{1}H^{+}$ with ^{115}In, any overestimation of the internal standard concentration would affect the results for all the other metals; (3) having to ablate through two layers of gel (i.e. 0.08 cm, instead of 0.04 cm) means that the above problem is likely to be worse because of the additional hydrogen going to the plasma thereby increasing the uncertainty; and (4) SPR-IDA resin is relatively expensive. Bearing the these points in mind, the dual layer approach presented by Warnken et al. is an additional step in the analysis that adds unnecessary uncertainty and expense to the analysis. Therefore we proposed the approach of Warnken et al. [13] to use ^{13}C, which is naturally present in resin-gel, as the internal standard. In other materials such as plant [14] or animal samples [15,16] ^{13}C was yet used. Second, his technique necessitated a defocusing of the beam to reduce the possibility of the laser ablating through the soft resin gel and into the underlying material (filter, glass, metal, etc.) which may in turn introduce contamination, while obtaining optimum sensitivity for the desired analyte. Our actual laser systems are different from the instrument used by Warnken et al. [11,12] and can be controlled much easier to avoid burning through the resin-gel layer. Third, in order to distinguish between individual ablation spots, the ablation cell needs to be flushed with the carrier gas in between ablations and this can result in very high analysis times and gas consumption [17]. Therefore, we will also optimize the line scan ablation mode, compare those results with the spot ablation mode results, and try to improve the spatial resolution. Line scan has been used for phosphorous on ferrihydride gels [17], however, no documented cases of line scans on SPR-IDA DGT gels for determining trace metals have been reported so far.

Finally, we will compare the performance of two LA-ICPMS systems, one at Lancaster Environment Centre (Lancaster University, Lancaster) and the other one at the Vrije Universiteit van Brussel, VUB (Brussels, Belgium) for the analysis of trace metals bound to SPR-IDA resin gels.

2. Materials and methods

2.1. Gel preparation

Agarose-polyacrylamide hydrogel consisting of 15% acrylamide (Merck, Belgium) and 0.3% agarose derived cross linker (DGT Research Ltd., UK) was used as a diffusive gel. To make 5 ml resin gel solution, 2.5 ml SPR-IDA resin (10%, CETAC Technologies Inc., USA) was added to the mixture of 2 ml acrylamide (40%, Merck, Belgium), 0.5 ml acrylamide cross-linker (2%, Merck, Belgium), 35 μl ammonium persulfate (1%, Merck, Belgium) and 10 μl N,N,N,N-tetraethylenediamine (TEMED, Merck, Belgium). The SPR-IDA resin is supplied pre-cleaned and no additional cleaning of the resin was carried out before its use. The solution was mixed well and cast between two glass plates with a spacer separating the plates. The assembly was placed in an oven at 45 °C for 1 h, and then the gel was hydrated in MilliQ water for at least one day until use.

2.2. Assembling DGT units for solution deployment

Resin gels were cut into 2.5 cm discs with a plexi-glass gel cutter and mounted on the moulding base. The diffusive gel was then placed on top of the resin gel and covered by a 0.45 μm Millipore Durapore membrane filter (HVLP, Millipore, Belgium). The cap was then placed on the moulding and pressed down to the bottom of the base to seal the probe.

2.3. Preparation of resin gel standards for laser ablation

Single-layer polyacrylamide gel standards were prepared by deploying DGT piston devices in sets of four into well-stirred $1\,\mathrm{mmol\,L^{-1}}$ $NaNO_3$ solutions containing five different concentration levels of Co, Ni, Cu, Zn, Cd, and Pb, which were added as acidified stock and metal salt standards ($1000\,\mathrm{mg\,L^{-1}}$), to give a final solution pH of 5. These experimental conditions were necessary to avoid losses from the deployment solutions, due to adsorption to the container walls, and from the formation of colloidal species. Every hour sub-samples (100 μl) were taken from the bulk solution and analysed by ICPMS.

The DGT pistons were removed from each of the deployment solutions after 4 h. Three of the above resin gel standards were eluted with 1 mL of $1\,\mathrm{mol\,L^{-1}}$ HNO_3 and analysed on the ICPMS against certified solution standards to quantify the mass of metal present on the resin gel. After elution still a small fraction of the metals remain trapped onto the resin gel and can only be liberated by a strong acid-oxidative treatment. This fraction varies from 14 to 20% of the total amount of metal trapped. Metal specific elution factors of 0.86 (Co), 0.86 (Ni), 0.84 (Cu), 0.81 (Cd), 0.80 (Pb) and 0.80 (Zn) determined by Warnken et al. [11] were applied to take into account the incomplete recovery of the trace metals from the resin gel by the acid. The mass of metal (M) on the resin gel is calculated using Eq. (1).

$$M = \frac{C_e(V_e + V_g)}{f_e} \tag{1}$$

where C_e, V_e and f_e are the metal concentration in the eluent, the volume of the eluent and the metal elution factor, respectively; V_g is the volume of the gel. From the mass of metal eluted from the resin gel, the bulk solution concentration can be calculated using Eq. (2):

$$c_{dgt} = \frac{M\Delta g}{DAt} \tag{2}$$

Table 1
Main operating parameters of the LA-ICP-MS system.

	Instrument condition		VUB	Lancaster
ICPMS	Instrument		Thermo Scientific X-Series 2	Thermo Scientific X-Series
	Forward power		1400 W	1400 W
	Reflected power		<1 W	1 W
	Cool Ar flow rate		L/min	L/min
	Auxiliary Ar flow rate		0.8 L/min	0.8 L/min
	Laser cell gas		He	Ar
	Carrier gas Ar flow rate			L/min
	Carrier gas mixture of He flow rate		L/min	–
	Carrier gas mixture of Ar flow rate		0.8 L/min	
	Pole bias		−1	0.2
	Hexapole bias		−4.0	−4.0
	Cones		Ni	Pt
	Oxide production (ThO/Th)		0.1–0.2%	<2%
	Detection mode		Dual	Dual
	Acquisition mode		TRA (time resolved analysis)	TRA (time resolved analysis)
	Isotopes monitored		^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{111}Cd, ^{208}Pb	^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{111}Cd, ^{208}Pb
	Internal standard		^{13}C	^{13}C
Laser ablation	Instrument		ESI New Wave UP-193FX Fast Excimer ArF	New Wave UP-213 (Nd-YAG)
	Wavelength		193 nm	213 nm
	Pulse length		4 ns	<4 ns
	Output energy		40% (energy: 8 mJ)	45–48%
	Ablation mode: spot	Spot size	100 μm	100 μm
		Repetition rate	10 Hz	20 Hz
		Dwell time	15 s	4 s
		Number of spots	20 per standard	20 per standard
	Ablation mode: line	Line width	100 μm	–
		Line length	1 mm	–
		Speed	50 μm s^{-1}	–
		Repetition rate	30 Hz	–

where c_{dgt} is DGT measured concentration, M is mass of metals, Δg is thickness of diffusive gel, D is the diffusive coefficient of solute in diffusive gel, A is the surface of the gel exposed to the bulk solution and t is deployment time.

The resin gels from the remaining DGT probes deployed above were immediately transferred onto new acid-washed 0.45-μm cellulose nitrate filters, similar to those that were used in the deployment, and dried using a commercial gel dryer (BioRad, Germany) at 60 °C for 24 h according to procedures presented by Warnken et al. [12]. Once dried, these single-layer DGT gel standards were cut into a suitable size and then mounted on a glass plate, using double sided tape, for laser ablation ICPMS analysis.

3. ICPMS instrumentation

The instruments used during this work were:

Lancaster Environment Centre: Thermo Elemental X-Series ICPMS connected to a New Wave UP-213 (Nd-YAG) Laser Ablation unit (UK), and using Ar for the laser cell and the plasma carrier gas.

VUB (ANCH): Thermo Elemental X-Series$^{\text{II}}$ ICPMS connected to a New Wave 193FX (Fast Excimer) instrument (UK), which incorporates an ATL Ex300Si ArF excimer laser, and using a mixture of He (from the laser cell) and Ar as the plasma carrier gas.

No defocusing of the laser beam was necessary (see Section 4) as it was the case with the former laser ablation instrument at Lancaster [12].

The PlasmaLab$^{\text{TM}}$ Version 2.0 software allows simultaneous control of the X-Series ICPMS and the laser ablation unit. The coupling with the laser was made via a New Wave Laser interface kit. Signal acquisition and processing for both spot and line ablation modes are made in the time resolved analysis (TRA) mode from Plasmalab$^{\text{TM}}$. In spot ablation mode the software uses an auto-search function over a user-defined acquisition time to identify the analyte peaks as counts per second, performs baseline corrections, and calculates peak areas as integrated counts per second. When line scan ablation mode was used, a number of time slices was defined after signal stabilization and the mean signal within each slice was reported.

The operating conditions for laser ablation-ICPMS analysis are summarized in Table 1. Spot ablation mode was applied by the LA-CPMS at Lancaster University while both spot and line scan ablation modes were applied by the LA-ICPMS at VUB. All analyses were carried out on the same resin gel standards.

4. Results and discussion

4.1. Elution results

The metal concentrations in solution calculated on the DGTs by using Fick's law can be compared to the concentrations directly measured on sub-samples of the solution. For one of the standard solutions the results are shown in Table 2. The comparison is generally very good for all metals, with a largest difference of 5% between the concentration calculated from the DGT piston and the concentration directly measured on a sub-sample of the solution.

Table 2
Trace metal concentrations of the deployment solutions: C_{dgt} is the concentration calculated from the DGT piston and C_s the concentration directly measured on a sub-sample of the deployment solution.

	C_{dgt} (μg/l)	C_s (μg/l)
Co	20.3 ± 0.35	20.5 ± 0.21
Ni	37.1 ± 1.1	37.6 ± 0.42
Cu	23.4 ± 0.30	23.6 ± 0.50
Zn	119 ± 6.0	117 ± 4.8
Cd	31.1 ± 0.77	29.0 ± 0.46
Pb	33.1 ± 0.49	31.6 ± 0.44

Triplicate analysis has been carried out on the gel eluent and the deployment solution.

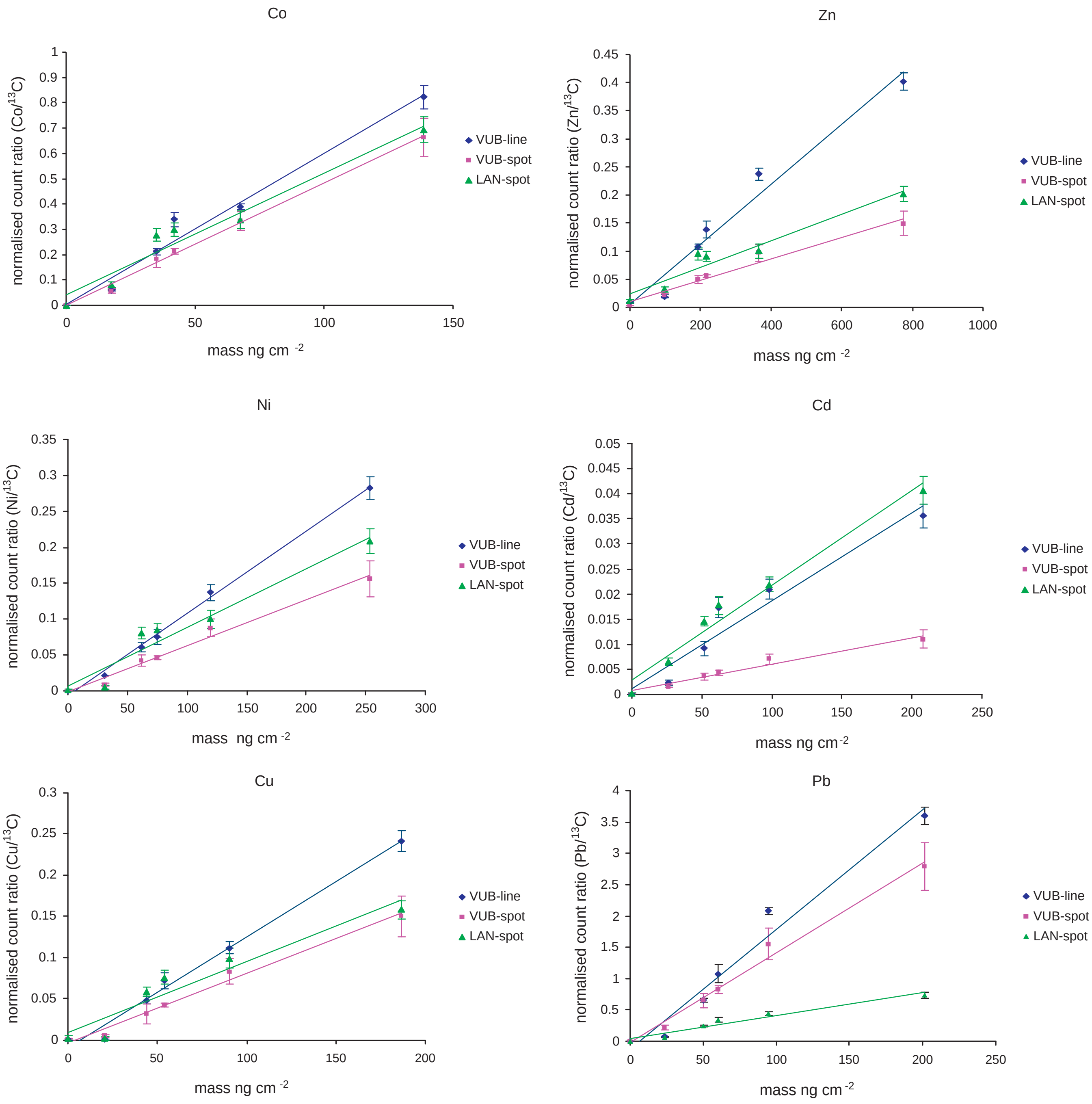

Fig. 1. The ratios of metal-counts to ^{13}C-counts assessed by LA-ICPMS are plotted versus the mass of metal per surface unit of resin gel assessed by ICPMS after elution (calibration graphs).

4.2. Inter-calibration exercise between two LA-ICPMS systems

The resin gels were analysed for metals and ^{13}C via spot ablation with both LA-ICPMS systems (Lancaster University and VUB). The settings are summarized in Table 1.

The laser ablation results obtained by the two LA-ICPMS systems are plotted as the normalized metal count rate (metal count rate divided by ^{13}C-count rate) versus the previously determined amount of metal per unit area of resin gel (ng cm^{-2}) (Fig. 1: spot ablation). Linear calibration graphs were obtained for the spot results from the Lancaster instrument (minimum correlation coefficient of 0.916 for Cu and maximum correlation coefficient of 0.975 for Cd) and from the VUB instrument (minimum correlation coefficient of 0.966 for Cu and maximum correlation coefficient of 0.996 for Co) (Table 3). For most metals the calibration graphs obtained with both LA-ICPMS systems are very similar except for Cd and for Pb. Laser ablation results obtained on blank resin gels allowed us to calculate the limits of detection (LODs) for each of the metals. The laser beam ablated 20 craters on the blank gel in order to calculate the LODs. The LOD was estimated as 3 times the standard deviation on the average metal-counts/^{13}C-counts for the blank, divided by the sensitivity and expressed in ng cm^{-2}. LODs for Cu and Pb are similar for both LA-ICPMS systems, while for Co, Ni and Zn they are lower for the VUB system and for Cd for the Lancaster system (Table 3). The LODs obtained by Warnken et al. [12] spot scans (data not shown) were higher than those obtained by

Table 3
Equations of the calibration curves and the limits of detections (LODs) for various trace elements measured by LA-ICPMS (VUB line scan ablation versus Lancaster spot ablation versus VUB spot ablation).

	Element	LODs (ng cm^{-2})	LODs[a] (μg L^{-1})	Equation	R[b]
VUB line scan	Co	0.055	0.039	$y = 0.006x$	0.977
	Ni	0.86	0.63	$y = 0.0011x$	0.997
	Cu	2.0	1.4	$y = 0.0014x$	0.984
	Zn	22	15	$y = 0.0005x$	0.962
	Cd	1.7	1.2	$y = 0.0002x$	0.975
	Pb	0.17	0.089	$y = 0.0196$	0.967
LAN spot scan	Co	0.36	0.25	$y = 0.0048x$	0.957
	Ni	6.3	4.6	$y = 0.0008x$	0.945
	Cu	3.7	2.5	$y = 0.0009x$	0.916
	Zn	94	66	$y = 0.0002x$	0.937
	Cd	2.4	1.7	$y = 0.0002x$	0.975
	Pb	0.30	0.16	$y = 0.0037x$	0.953
VUB spot scan	Co	0.078	0.056	$y = 0.0048x$	0.996
	Ni	1.2	0.86	$y = 0.0006x$	0.966
	Cu	4.1	2.8	$y = 0.0008x$	0.966
	Zn	24	16	$y = 0.0002x$	0.986
	Cd	5.1	3.5	$y = 0.00005x$	0.986
	Pb	0.20	0.11	$y = 0.00143x$	0.987

[a] These LODs are the corresponding concentrations of metals in porewaters for a DGT deployment time of 4 h at 20 °C.
[b] R value is slope of the regression line obtained by plotting count ratio vs mass (ng cm^{-2}).

both LA-ICPMS systems for Co, Ni, Cu, Cd and Pb, whereas the LOD for Zn was lower.

It is important to ensure that the laser does not ablate through the resin gel and vaporise material below. The metal content of the backing membrane cannot be guaranteed nor can it be shown to be uniform and any ablation of this membrane can lead to erroneous results. In order to observe if there was any ablation through the resin gel, a back-up layer of diffusive gel was infused with ^{115}In and laid underneath the resin gel. This stack of diffusive and resin gel was dried together prior to ablation and analysed. No signal for ^{115}In was observed during this exercise, which suggests that the laser power used for the above analysis was not too high. The New Wave laser ablation units are equipped with an microscope head that allows close inspection of the sample before during and after the ablation, and the precise placement of the ablation locations. A subsequent visual inspection of the groove created by the laser also confirmed that the laser beam was not burning through the resin gel during ablation.

4.3. Optimisation of the line scan ablation

In line scan ablation mode, the laser continuously ablates the resin gel at a predefined speed and with a predefined power. As a first exercise we tested the homogeneity of the standard resin gels. Several line scans were performed and showed a very good homogeneity of the metal amounts in the gel. The sensitivity of the method was investigated by observing the ^{13}C count rate at different scan speeds and power. The laser output energy (%) and repetition rate (Hz) were found to be the two key parameters that combine to determine detector signal (count rate) in line scan ablation. These results, which are all obtained on the same resin gel, are shown in Table 4. The best sensitivity (without ablating through the resin gel) was obtained at a line speed of 50 μm s^{-1}, output energy of 40% and repetition rate of 30 Hz. A visual inspection of the gel following ablation using laser output energy of 40% and a repetition rate of 40 Hz showed that the laser beam had burned through the resin layer.

Table 4
Optimisation of line scan ablation for laser ablation system.

Output (%)	Repetition rate (Hz)	Counts for C^{13}
30	10	39,000 ± 1000
40	10	52,000 ± 1600
40	20	100,000 ± 2800
40	30	160,000 ± 2300
40	40	220,000 ± 3000

In order to ensure that the laser beam does not cross through the resin gel and ablate the material below, the diffusive gel-resin gel stack analysed above was analysed again using the line scan. No ^{115}In was observed during this test.

4.4. Application of the line scan ablation

Each of the five resin gel standards was analysed by LA-ICPMS using the optimal line scan ablation described above. For each of the metals and for ^{13}C, count rates were simultaneously assessed over a length of 1.0 mm in one of the resin gel standards. All acquisitions (every 25 ms) of the logarithmic normalised ratio (metal/^{13}C) are shown in Fig. 2 for the fourth resin gel standard: the signal becomes stable after 250 ms (at acquisition point 11) and remains stable during 2.0 s (until acquisition point 93). For this stable region of the line scan, the average count rate was calculated. Under these conditions, the resolution goes down to 10 μm. However, if this high resolution is not needed, the acquisition time can be increased. For example, doubling the acquisition time (from 25 ms to 50 ms) would double the spatial resolution (from 10 μm to 20 μm).

For each metal, the average normalised count ratio of metal/^{13}C is plotted against the amount of metal (ng) measured after elution of the resin and divided by the surface of the resin gel layer (Fig. 1: line scan ablation). The linearity of the calibration curves is very good and the correlation coefficient varies between 0.962 for Zn and 0.997 for Ni (Table 3). Line scans of 1.0 mm length (about 125 acquisition point obtained) were also performed on the same blank resin gel and the average normalised count ratio of metal/^{13}C was calculated in a similar way as for the standard resin gels. As for the spot ablation, the limit of detection (LOD) was also estimated as three times the standard deviation on the average normalised count ratio of metal/^{13}C for the blank, divided by the sensitivity. LOD values are summarized in Table 4: Co has the lowest LOD (0.055 ng cm^{-2}) and Zn has the highest LOD (22 ng cm^{-2}).

When we compare the line scan ablation results with those obtained from the spot ablation, all line scan LODs are lower than those obtained by the spot ablation. However, for some of the metals the difference is rather small (Table 3).

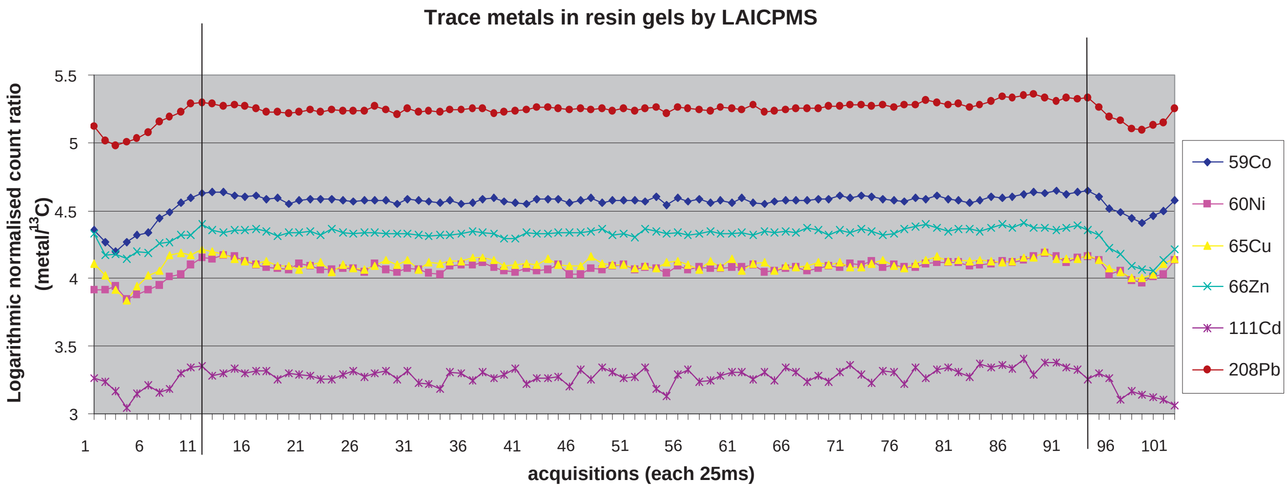

Figure 2. Laser line ablation ICPMS acquisition (each 25 ms): logarithmic normalized count ratio of metal/^{13}C.

All spot ablation and line scan ablation LODs expressed in ng cm^{-2} are also converted in expected bulk concentrations for DGT settings of 4 h of exposure, 0.5 mm diffusive layer thickness, 3.14 cm^2, the area of the DGT device exposure window, and the appropriate trace metal diffusion coefficient at 20 °C (Table 3).

The line scan ablation mode is also somewhat faster than the spot ablation mode. A simple calculation using for the spot mode 40 spots of 500 μm (100 μm crater and 400 μm space in between craters) which means a total length of 2 cm, 4 s dwell time/spot, 10 s washout time between 2 spots and for the line scan mode a speed of 50 μm s^{-1} for a same length of 2 cm results in a 30% faster analysis time with the latter mode.

5. Conclusion

Laser ablation ICPMS is a very convenient and non-destructive method for analysing trace metals in the resin gels of DGT. It allows considerably higher spatial resolution analysis of resin-bound metals than slicing. The spot ablation used by the LA-ICPMS at Lancaster University and at VUB gave comparable results for Co, Cu, Ni and Zn. The LOD varies between 0.078 ng cm^{-2} for Co and 94 ng cm^{-2} for Zn for a crater size of 100 μm The line scan ablation allows, however, a higher spatial resolution that can go down to 10 μm for an even better sensitivity than for the spot ablation. Indeed, LODs vary between 0.055 ng cm^{-2} for Co and 22 ng cm^{-2} for Zn at a resolution of 10 μm.

Compared to earlier work [12], we improved the method on following points: (1) internal standardization of the samples is necessary to correct for fluctuations of the laser and the ICPMS and it is common to use In as internal standard. This is a laborious procedure when analysing a resin-gel, because it involves infusing the underlying layer with In. Therefore, In was replaced by ^{13}C, which is naturally present in resin-gel, as internal standard and (2) our actual laser systems can be controlled much easier than the older laser system at Lancaster to avoid burning through the resin-gel. In addition, when the laser at VUB was operated in line scan ablation, it was very easy to arrange scan speed and laser power to avoid burning through the gel. Hence, our lasers need no longer to be defocused as it was before.

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