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**Dried droplet calibration approach for the analysis of solid samples through Laser
Ablation – Inductively Coupled Plasma Mass Spectrometry**

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A novel calibration method has been developed for the bulk analysis of solid samples through laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS). The method has been called dried droplet calibration approach (DDCA). This procedure is thus based on the deposition of a small aqueous standard volume (*c.a.*, 1 μL) on the flat surface of a solid sample. Then, the solvent is allowed to completely evaporate at room temperature and the solid residue is finally ablated. The implicit assumptions of the DDCA are that: (i) a single raster is enough to fully ablate the solid layer originating from the evaporation of the standard; and, (ii) the solid residue does not affect the sample ablation yield. Both hypothesis have been verified in the present work. Therefore, several rasters have been done on the solid residues and the generated signals have been obtained by using an ICP-MS spectrometer. The calibration lines are obtained by plotting the sum of intensities for a given residue (corresponding to a given analyte concentration) versus the analyte ablated mass per laser shot. This method is similar to a standard additions procedure and, hence, the analyte mass ablated from the sample per laser shot has been obtained by extrapolating the obtained straight line to the y-axis zero value. The method has provided accurate concentration results for a glass CRM and three different catalysts employed for petroleum refining purposes, prepared as fused beads. The obtained results have demonstrated that it is possible to overcome significant matrix effects by applying the DDCA.

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Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is widely used for the direct analysis of solid samples combining unique advantages over traditional methods such as solid sample dissolution or XRF.¹⁻³ However, its main analytical problem lies in the calibration step.⁴ In fact, standards used for external calibration should be closely matrix matched to the sample. In some instances, the elemental fractionation caused during aerosol formation, its transport to the ICP and the analyte vaporization and ionization in the ICP plasma leads to inaccurate results. Furthermore, all these processes are significantly affected by the sample matrix.⁴⁻⁶

Unfortunately, matrix-matched solid standards are often not available and they can be prepared as fused beads, pelletized solids^{4,5,7,8} or by sol-gel formation.^{9,10} O'Reilly et al.¹¹ developed a method in which matrix matched standards were prepared by immersion in a methanol containing standard. Then, this solvent was evaporated to yield the solid standard. The precision of the method was improved by using rhodium as internal standard. In any case, the preparation of matrix matched standards can be time consuming, expensive.⁴⁻⁷ and it may degrade the spatial integrity of the sample.

Additional approaches include merging the aerosols generated with a conventional sample introduction system with those produced through laser ablation^{6,7,12-14} or to use a spinning sample platform containing both the sample and the standard that is spun during the ablation process.¹⁵ As a result, the aerosols generated through the ablation of the sample and the standard are combined inside the ablation cell.

In previous published works, a method consisting of the deposition of a liquid solution on a solid support, its drying and its further ablation was suggested for the analysis of complex samples¹⁶⁻²³ thus giving rise to the so-called dried blood spots (DBS) or dried urine spots (DUS) sample methods. Several inert supports have been tested for deposition and dispersion of both samples and aqueous standards such as PTFE, glass slide, filter paper²¹ and cellulose.²⁴ Contrarily to what has been previously demonstrated,^{25,26} the use of carbon as internal standard provided accurate results in the latter case.²⁴

However, with these methods, chromatographic effects responsible for the inhomogeneous analyte distribution through the droplets must be taken into account. In order to overcome this problem and avoid sample diffusion and dilution in the support, small precut paper pieces can be employed as demonstrated by Aramendía et al.²² As an additional advantage, an internal standard can be easily incorporated to the system either to the liquid sample before its deposition or directly to the solid support.²³ This straightforward methodology is also useful for localized analysis.^{27,28}

Methods such as those previously discussed, only applied to the direct bulk analysis of liquid samples could be easily adapted to the direct analysis of solid materials. The goal of the present work was thus to develop, for the first time, a novel calibration method for LA-ICP-MS bulk analysis of solid materials based on the deposition of a series of aqueous standards on the sample surface. The remaining residue after the complete evaporation of the droplet was ablated together with the sample. This approach has been referred to as dried droplet calibration approach (DDCA). The main novelty of the present methodology lies in the fact that the liquid

standard is deposited directly on the solid sample and dried from there. Hence, unlike previously described dried droplet methods, the DDCA is based on a standard additions procedure used for the direct analysis of solid samples. To demonstrate its suitability, the new method has been applied to the analysis of a glass certified reference material (CRM) and fused beads containing a given fraction of catalysts commonly employed in the refining process.

Experimental

Chemicals and samples

The solutions used to obtain the calibration line were prepared from an ICP multielement standard solution IV (Merck IV, Merck KGaA, Darmstadt, Germany) containing 1,000 mg element L⁻¹ and two 1,000 mg L⁻¹ single element stock solutions of V and Mo (Merck, Darmstadt, Germany). Ultra-pure water prepared from a Milli-Q system (R < 18.2 MΩ) obtained with a Millipore water purification system (El Paso, TX, USA) was used for all experiments. 1 μL of these standard solutions was manually deposited on the solid sample surface by means of an automatic pipette (Eppendorf, Hamburg, Germany). The deposited droplets were evaporated until dryness in a hood at room temperature. A glass petri-dish was employed to avoid possible contamination. Then, the resulting solid residues were laser ablated.

The selected solid samples were two alumina catalysts employed in petroleum refining processes (one of them, catalyst 1, was a CoMo based material), a spent zeolite and a glass Standard Reference Material NIST 612.

Sample preparation

In order to prepare the samples corresponding to catalysts, 10.3 g of lithium tetraborate were blended with 0.2 g of KI (anti wetting agent), 1-1.5 g of LiNO_3 (employed as oxidizing agent to prevent losses of volatile metallic species) and 1.5 g of catalyst. The homogenized mixture was put inside platinum discs and inserted into a muffle. The fusion program consisted in a first oxidation step at 610°C for 7 minutes. Then, the temperature was raised up to 1150°C for 2 minutes and kept at this level for 4 minutes. Finally, the fused samples were cooled for 5 minutes. After this sequence, the obtained fused bead was ready for the analysis.

The accuracy of the DDCA method was tested by analyzing the beads through an acid microwave assisted sample digestion step. The fused beads were grounded; 250 mg were weighed with a precision of ± 0.1 mg and transferred to a microwave digestion vessel to which 9 mL of HCl 37% and 1 mL of HNO_3 65% (Surpapur®, Merck KGaA, Darmstadt, Germany) had been added. The samples were digested using a microwave oven Start D (Milestone, Sorisole, Italy) setting the temperature at 220 °C for 15 min. The solutions obtained were transferred to graduated flasks and diluted to 25 mL with Milli-Q water.

Instrumentation

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A CETAC Technologies LSX-213 G2+ system (CETAC, Omaha, USA) was employed that generated a Q-switched frequency-quintupled (213 nm) Nd:YAG laser. The ablation took place inside a two volume ablation cell (HELEX). The system contained a CCD camera that allowed real-time observation of the ablation process. The laser operating conditions were optimized in terms of both sensitivity and absence of segregation effects for the evaluated samples (see Table 1).

The laser ablation system was coupled to a 7700x Agilent ICP-MS spectrometer (Agilent, Santa Clara, USA). In order to remove polyatomic spectral interferences the collision cell mode was used. The experimental conditions are summarized in Table 1.

A Hitachi S-3000N Secondary Electron Microscope (SEM) was employed to characterize the shape and dimensions of the obtained rasters for the different tested samples.

Development of the quantification method

The DDCA was based on the initial determination of the sample ablated mass. To obtain this parameter, the sample was weighed before the analysis with a Mettler Toledo balance (precision of $\pm 1 \mu\text{g}$). Once the sample was ablated using a known number of laser shots (*i.e.*, after the analysis), the ablation cell was carefully disassembled and the sample was led to the micro-balance in a sealed glass container to avoid external contamination. The mass difference yielded the total ablated sample mass (M_s). This magnitude was divided by the total number of pulses thus giving rise to the ablation rate.

The total number of pulses, N_p , were easily obtained by applying equation 1:

$$N_p = \frac{N_r L_r}{v_s} f \quad (1)$$

where N_r was the number of rasters selected to ablate the solid residue, L_r the raster length, f the shot frequency and v_s the scan rate.

Therefore, the sample ablated mass per pulse, M_p , was given by the following mathematical relationship:

$$M_p = \frac{M_s}{N_p} \quad (2)$$

Besides, the mass of analyte ablated from each dried droplet, m_A , could be obtained by means of:

$$m_A = C V S_A \quad (3)$$

where C was the analyte concentration in the liquid solution, V the volume of the deposited droplet (*i.e.*, 1 μ L) and S_A the percentage of ablated area of the solid residue. The latter parameter, in turn, could be obtained from the laser beam diameter ($\emptyset$) and the diameter of the dried droplet (D) by considering an average raster length:

$$S_A = \frac{N_r \emptyset}{D} \quad (4)$$

The raster width was measured by means of a scanning electron microscope. It was experimentally found that for a 150 μ m laser beam diameter, the actual raster width was 158 ± 8 .

As the number of pulses employed to ablate a given dried droplet (N_p') could be calculated by applying Equation 1, it was also possible to determine the mass of analyte ablated per pulse from a single droplet (m_A/N_p'). Note that N_p was higher than

N_p' , because it was necessary to ablate a high enough mass of sample to determine its mass by direct weighing.

Therefore, a calibration line was obtained by plotting the integrated intensity versus the analyte mass ablated from each one of the solid residues per laser pulse. Note that the point 0 in the x-axis corresponded to the integrated intensity for the sample with no solid residue. Therefore, by extrapolation of the calibration line, it was possible to determine the analyte ablated mass initially contained in the sample per laser pulse (m_s) .

The last step of the present quantification strategy was to determine the analyte concentration in the sample (C_A^S) by means of the following mathematical relationship:

$$C_A^S = \frac{m_s}{M_p} \tag{5}$$

Once the solid residues were deposited on the sample surface, a non-homogeneous spatial analyte distribution within the dried droplet was observed. This likely corresponded to the interactions established between the analytes and the solid surface and/or the preferential accumulation/precipitation of elements at particular sample locations. These phenomena led to signal spikes when the solid residue was ablated. Therefore, in order to perform calibration, it was necessary to ablate a significant surface of the dried droplet. Three different approaches were thus assayed: (i) ablation of the totality of the residue surface; (ii) ablation of a fraction of the dried droplet as representative as possible of the whole residue; and, (iii) ablation of only a line-scan across the entire dried droplet. The intensities obtained during these

experiments were integrated and this parameter (I_i) was divided by the droplet ablated surface and taken as the ordinate value in the calibration lines.

Results and discussion

The strategy followed in the present work to achieve the proposed goals is schematized in Figure 1. After previous optimization of the laser parameters, the DDCA was developed demonstrating the linear relationship existing between the analytical signal and the analyte mass ablated per laser shot. Afterwards, the influence of the solid residue on the sample ablation yield was studied. Once the matrix effects were characterized, the DDCA was applied to the analysis of a CRM and real samples (Figure 1).

Optimization of the laser operating conditions

An univariate optimization of the laser operating conditions was carried out in terms of ICP-MS sensitivity. The variables studied were: shot number frequency, beam diameter and pulse energy. It was observed that an increase in the laser shot frequency led to a growth nearly linear of the intensity. As regards the beam diameter, the increase in sensitivity was exponential for values of this laser variable going from 10 to 150 μm . The higher sample ablated mass was in the origin of these trends. For a 4 μm laser, the sensitivity was actually low and it was possible to detect only major elements. The third evaluated parameter was the laser energy and it was realized that the signal

initially increased with this variable and it plateaued above a given value. This widely described behavior can be due to a degradation in the laser-sample interaction that may be caused by the absorption of energy by the plasma generated at the sample surface and/or the ablated material.^{29,30} In our case, the situation was complex, because the sample nature affected the optimum laser energy. Thus, the optimum energy values were 1.8 – 2.7, 2.7 – 3.6 and 3.2 – 3.6 mJ pulse⁻¹ for the alumina based catalyst, the blank (lithium tetraborate) and the spent zeolite, respectively. In the present work, the laser energy was kept at 60% (2.7 mJ pulse⁻¹) for carrying out the catalysts analysis by LA-ICP-MS, because it represented an average optimum value.

Dried droplet ablation

Figure 2 shows the calibration lines obtained for vanadium following the three ablation methods mentioned in the experimental section. For the sake of clarity, the patterns are also schematized. In this case, the x-axis corresponded to the analyte ablated mass from each dried droplet per pulse (m_A/N_p') and the y-axis corresponded to the I_i per ablated surface area. It was clearly noticed that a linear relationship was obtained for the three different approaches what demonstrated the potential of this simple procedure for elemental quantification purposes. By comparing the three calibration lines, it was verified that the analyte mass fraction at the center of the droplet was higher than in its periphery because the slopes for one and three rasters were higher at the residue center than when considering thirteen rasters. In the present work, the entire residue was ablated. In order to further shorten the analysis time, additional simplified

methods (*i.e.*, ablating only a representative fraction of the sample surface) could be evaluated as a function of the accuracy sought.

In order to test the repeatability of the measurement method, five 1 μL droplets were deposited at different locations on the sample surface by means of an automatic pipette. These droplets corresponded to a 20 $\mu\text{g mL}^{-1}$ multielemental standard solution. The entire solid residues were ablated and the integrated signal values were compared. As Table 2 reveals, in the case of four representative analytes the RSD (%) values were included within the 8.8 to 15% range depending on the element tested.

Effect of the solid residue on the sample ablation yield

The suitability of the DDCA was based on the assumptions that the analyte contained in the dried droplet was completely ablated on the one hand, and that there was not any influence of the solid residue on the sample ablation yield, on the other. Therefore, a first study was devoted to evaluate the effect of the laser operating conditions in order to verify that the dried droplets were completely ablated after the first laser scan. In this study, a droplet corresponding to an aqueous 20 $\mu\text{g mL}^{-1}$ multielemental standard was deposited on an alumina based catalyst. Four consecutive rasters were performed on same area of the dried droplet and another four on a sample clean area, *i.e.*, with no droplet. This experiment allowed us to verify the influence of the analyte diffusion towards the sample, because depth profiles were actually obtained.

Under the operating conditions indicated in Table 1, the signal measured for the first raster on the dried droplet was much higher than that encountered in absence of solid residue (Figure 3 and Table 3). When the second raster was completed at the same location, the V and Pb signals corresponding to the area where the droplet was initially deposited was still significantly higher than that for the sample without droplet (Figure 3 and Table 3). These results suggested that a fraction of elements had diffused from the droplet to the sample and/or, once the sample was ablated, a portion of the particles were redeposited on the sample groove created by the laser. For the third and fourth rasters (Figure 3, Table 3), the vanadium signal corresponding to the area where the droplet was deposited was of the same order as that corresponding to the area of the sample without droplet. In order to improve the dried droplet ablation yield in the first raster, the scan rate was lowered with respect to that indicated in Table 1. It was verified that, for a $25 \mu\text{m s}^{-1}$ scan rate, the integrated signals when performing the second raster represented 6.2% and 3.5% that measured from the first raster for V and Pb, respectively. Therefore, under these conditions, a single laser raster was considered to be enough to completely ablate the analyte deposited as a dried droplet.

Another point that had to be verified to test the suitability of the DDCA was whether the solid residue affected the sample ablation efficiency. A droplet corresponding to a $20 \mu\text{g mL}^{-1}$ multielemental solution containing neither vanadium nor molybdenum was deposited on the CoMo catalyst. The remaining residue after droplet evaporation was subsequently ablated and the ionic signals for these two elements were registered. Signals were compared against those measured when ablated a sample surface that did not contain any solid residue. F and t statistical tests

were applied and the results revealed that the signals obtained for the two situations were not significantly different ($t_{\text{calculated}} = 1.74$ for V and $t_{\text{calculated}} = 0.52$ for Mo, $t_{\text{tabulated}} = 2.00$) regardless the presence of solid residue. In other words, the sample ablation yield was not modified by the presence of the solid residue formed after evaporation of the droplet initially deposited on the sample surface.

Influence of the matrix composition

In order to assess the extent of the interferences caused by changes in the sample nature, three different catalysts were analyzed: two alumina-based catalysts and a zeolite. The corresponding values of the ablated mass were determined for the four samples. This parameter was: 10, 9 and 77 (ng of sample)/(laser spot) for the alumina-based catalyst 1 and 2 and the zeolite samples, respectively. This fact confirmed the influence of the sample matrix on the ablation process.

An additional investigation was performed in which the craters generated at the surface of the catalysts were observed by means of SEM (Figure 4). Interestingly, as previously stated for other samples,^{31,32} the crater appearance depended on the ablated sample. Thus, for a 100 μm laser beam diameter, the alumina-based catalyst (Figure 4.a) exhibited a crater perfectly defined apparently surrounded by a rather unaltered sample surface. Under these conditions, particle deposits were not clearly observed and the bottom of the crater acquired a porous structure. Previous observations related with the aerosol formation from alumina based catalysts

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anticipated the appearance of solid porous particles resulting from the condensation of vaporized material.³³ However, in the case of the $\text{Li}_2\text{B}_4\text{O}_7$ sample (Figure 4.b), solid deposits were evident whereas the crater bottom evidenced a partial sample melting. Finally, the image of the crater corresponding to the spent zeolite (Figure 4.c) clearly evidenced the formation of particle deposits around the crater and sample melting. By a closer inspection of these craters (data not shown) it was found that the particle deposits were very different between these two samples. Thus, for the tetraborate sample, a big amount of stratified scale shaped particles were found whose size did not exceed 10 μm . Meanwhile, the material settled around the crater of the latter sample consisted of mainly amorphous particles although some of them had a prism structure. Interestingly the particles deposited in this case were quite dimensionally regular (2.5 μm length, 1 μm base approximately). These data collectively demonstrated that the laser-sample interaction was different as a function of the catalyst considered, hence anticipating the existence of a matrix effect.

Droplets of the same aqueous standard (20 $\mu\text{g mL}^{-1}$) were deposited on the samples surfaces and the resulting solid residues were ablated. The integrated intensities are summarized in Figure 5. It may be observed that this parameter was higher when considering the aluminosilicate sample as compared to the alumina based catalysts. Meanwhile, the blank provided intermediate analytical signals. This trend was interesting, because it demonstrated that the substrate on which the solid residue was formed had a direct impact on its ablation, even if the chemical nature of this deposit remained unaltered for all the samples. It was also noticed that, although the zeolite sample provided an ablation mass per laser shot around 8-9 times higher than the alumina-based catalyst, the signal relative factor was close to 3-4. These

discrepancies could be assigned to a lower aerosol transport efficiency and/or analyte ICP ionization yield in the case of the former catalyst. The existence of a matrix effect was thus clearly evidenced from the data shown in Figures 4 and 5.

Therefore, a simple method such as that described in the present work would be useful to compensate for matrix effects, because a calibration line would be obtained for every particular sample. Furthermore, the DDCA is based on a standard addition procedure that eliminates the contribution of the matrix to the finally obtained analytical concentration. Figure 6 shows an example of the calibration line obtained when applying the DDCA (e.g., ^{60}Ni Integrated intensity = $4 \times 10^9 \text{ m}_A/\text{N}_p' + 4 \times 10^6$, $R^2=0.9965$). The analyte concentration was obtained by extrapolation of the line (see the empty arrow in [Error! Reference source not found. Figure 6](#)) and applying equation 5.

Accuracy of the calibration methodology

Once it was demonstrated that the presence of the solid residue did not affect the sample ablation and that a single raster was enough to ablate entirely the analyte layer deposited on the sample, the calibration method described in the experimental section could be applied.

The suitability of the DDCA was tested by analyzing a certified reference glass sample (NIST 612). Table 4 summarizes the obtained results. Two series of experiments were carried out in order to test the repeatability of the developed method. It was observed that, taking into account the confidence intervals, the experiments performed at two sample locations provided concentrations that were not significantly

different ($\alpha = 0.05$, $t_{\text{calculated}}$ for the different elements= 0.5-1.4, $t_{\text{tabulated}} = 2.306$). A statistical test was performed taking into account the certified values, the measurement results and their respective uncertainties.³⁴ The expanded uncertainties U_{Δ} were larger than the differences between the certified and measured values (Δ_m). The measured mean values were therefore not significantly different from the certified ones. Only the measured mean values for Mn and Co were somewhat different from the certified value. In this case, sensitivity was low what could account for these results.

Analysis of catalyst fused beads

In order to further test the accuracy of the developed calibration method, several samples were analyzed and the obtained concentrations were compared against those encountered through a microwave acid digestion procedure. The corresponding values are gathered in Table 5. An F and t statistical test was applied and the results confirmed that there were not statistically significant differences between the concentrations found by applying the DDCA and those obtained following the microwave digestion process ($t_{\text{calculated}}$ for the different elements= 0.08-2.3, $t_{\text{tabulated}} = 2.447$, $\alpha = 0.05$). Only for three out of 20 situations (Cu found in the alumina based catalyst 1, Ni contained in the alumina based catalyst 2 and Cr determined in the zeolite) the obtained concentrations by means of the DDCA differed with respect to those found following the microwave digestion method. In conclusion, the DDCA was able to overcome the matrix effects.

Conclusions

The deposition of an aqueous standard on a solid sample and its further evaporation until dryness permits to develop, for the first time, a novel dried droplet calibration approach (DDCA) for the direct analysis of solid samples through LA-ICP-MS. Advantages of the DDCA over the existing procedures include the removal of matrix effects, the simplicity of the experimental procedure, the increased sample analysis speed and the reduced cost. Accurate values have been obtained with four different solid materials thus indicating that the DDCA can be a promising alternative to overcome the most important problem in LA analysis, namely the lack of suitable standards.

Elemental fractionation is another serious problem suffered by laser ablation. The DDCA may overcome this problem as well, although additional studies must be carried out in this field, since it has been recognized that the analyte chemical form may have an important effect on the ablation efficiency and, hence, on the analytical results.

Several points should be taken into consideration regarding the applicability of the DDCA as it was described in the present work: *(i)* obviously, the concentration range of the standards should be carefully selected to cover the analyte concentration in the sample; *(ii)* the method is based on the calibration line extrapolation and, hence, the signal measurements should be as precise as possible. On this subject, the use of an appropriate internal standard can be envisaged; *(iii)* the method is not suitable to perform quantitative spatially resolved analysis; and, *(iv)* the interaction of the analyte with the solid surface may vary according to the sample physical and chemical

properties. These points are currently under study and will be the subject of further reports.

References

1. B. Fernández, F. Claverie, C. Pécheyran, O. F. X. Donard, *TrAC Trends Anal. Chem.*, 2007, **26**, 951–966.
2. R. E. Russo, X. Mao, J. J. Gonzalez, V. Zorba, J. Yoo, *Anal. Chem.*, 2013, **85**, 6162–77.
3. F. A. Orellana, C. G. Gálvez, M. T. Roldán, C. García-Ruiz, *Trends Anal. Chem.*, 2013, **42**, 1–34.
4. A. Limbeck, P. Galler, M. Bonta, G. Bauer, W. Nischkauer, F. Vanhaecke, *Anal. Bioanal. Chem.*, 2015, **407**, 6593–6617.
5. N. Miliszkiewicz, S. Walas, A. Tobiasz, *J. Anal. At. Spectrom.*, 2015, **30**, 327–338.
6. D.B. Aeschliman, S.J. Bajic, D.P. Baldwin, R.S. Houk, *J. Anal. At. Spectrom.*, 2003, **18**, 1008–1015.
7. J. S. Becker, C. Pickhardt, and H-J. Dietze, *J. Anal. At. Spectrom.*, 2001, **16**, 603–606.
8. A. Barats, C. Pécheyran, D. Amouroux, S. Dubascoux, L. Chauvaud, O.F.X. Donard, *Anal. Bioanal. Chem.*, 2007, **387**, 1131–1140.
9. M. Martínez, C. Arnaudguilhem, R. Lobinski, B. Bouysiere, M. Caetano, J. Chirinos, *J. Anal. At. Spectrom.*, 2012, **27**, 1007–1011.
10. M. Viger, J.-F. Gravel, D. Brouard, D. Beauchemin, D. Boudreau, *Anal. Chem.*, 2005, **77**, 706–710.
11. J. O'Reilly, D. Douglas, J. Braybrook, P.-W. So, E. Vergucht, J. Garrevoet, B. Vekemans, L. Vincze, H. Goenaga-Infante, *J. Anal. At. Spectrom.*, 2014, **29**, 1378–1384.
12. X. Mao and R. E. Russo, *J. Anal. At. Spectrom.*, 1997, **12**, 177–182.
13. D. B. Aeschliman, S. J. Bajic, D. P. Baldwin, and R. S. Houk, *J. Anal. At. Spectrom.*, 2003, **18**, 872–877.

14. D.N. Douglas, J. O'Reilly, C. O'Connor, B.L. Sharp, H. Goenaga-Infante, *J. Anal. At. Spectrom.*, 2016, **31**, 270-279.
15. F. Claverie, J. Malherbe, N. Bier, J.L. Molloy, S.E. Long, *Anal. Chem.*, 2013, **85**, 3584-3591.
16. H-F. Hsieh, W-S. Chang, Y-K. Hsieh and C-F.Wang, *Analytica Chimica Acta*, 2011, **699**, 6-10.
17. H-F. Hsieh, W-S. Chang, Y-K. Hsieh and C-F.Wang, *Talanta*, 2009, **79**, 183-188.
18. W. Nischkauer, F. Vanhaecke, S. Bernacchi, C. Herwig and A. Limbeck, *Spectrochim. Acta Part B*, 2014, **101**, 123-129.
19. T-M. Do, H-F. Hsieh, W-C. Chang, E-E. Chang, C-F. Wang, *Spectrochim. Acta Part B*, 2011, **66**, 610-618.
20. L.Yung, R.E. Sturgeon and Z. Mester, *Anal.Chem.*, 2005, **77**, 2971-2977.
21. U. Kumtabtim, A. siripinyanond, C. Auray-Blais, A. Ntwari and J.S. Becker, *Int. J. Mass Spectrom.*, 2011, **307**, 174-181.
22. M. Aramendia, L. Rello, F. Vanhaecke and M. Resano, *Anal. Chem.*, 2012, **84**, 8682-8690.
23. M. Aramendía, L. Rello, S. Bérail, A. Donnard, C. Pécheyran, M. Resano, *J. Anal. At. Spectrom.*, 2015, **30**, 296-309.
24. M.A.G. Nunes, M. Voss, G. Corazza, E.M.M. Flores, V.L. Dressler, *Anal. Chim. Acta*, 2016, **905**, 51-57.
25. D.A. Frick, D. Günther, *J. Anal. Atomic Spectrom.*, 2012, **27**, 1294-1303.
26. J.L. Todolí, J.M. Mermet, *Spectrochim. Acta, Part B*, 1998, **53**, 1645-1656.
27. M. Bonta, B. Hegedus, A. Limbeck, *Ana. Chim. Acta*, 2016, **908**, 54-62.

28. M. Shariatgorji, A. Nilsson, M. Bonta, J. Gan, N. Marklund, F. Clausen, P. Källback, H. Loden, A. Limbeck, P.E. Andrén, *Methods*, 2016, **104**, 86-92.
29. R. E. Russo, *Appl. Spectrosc.*, 1995, **49**, 14A-28A.
30. M. E. Shaheen, J. E. Gagnon, and B. J. Fryer, *J. Appl. Phys.*, 2013, **114**, 1-8.
31. M. E. Shaheen and B.J. Fryer, *Laser Part. Beams*, 2012, **30**, 473-479.
32. J. Mikova, J. Kosler, H. P. Longerich, M. Wiedembeck and J.M. Hanchar, *J. Anal. At. Spectrom.*, 2009, **24**, 1244-1252.
33. G. Alloncle, N. Gilon, C. Legens, C.P. Lienemann, B. Rebours, L. Sorbier, S. Morin, R. Revel, *Appl. Surf. Sci.*, 2009, **255**, 8978-8985.
34. T. Linsinger, ERM Application Note 1, European Commission - Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), 2010.

Table 1. Optimized operating conditions

Ablation system	
Ablation frequency/ Hz	20
Spot size/ μm	150
Scan rate/ $\mu\text{m s}^{-1}$	50
Pulse energy (60%)	2.7 mJ pulse ⁻¹
Gas flow rates He / L min ⁻¹	0.5 and 0.3
ICP-MS system	
RF power/ KW	1.55
Carrier gas/ L min ⁻¹	0.3
Cell Collision (He)/ mL min ⁻¹	4.3
Isotopes measured	¹¹ B, ²⁷ Al, ⁵¹ V, ⁵² Cr, ⁵⁵ Mn, ⁵⁶ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁸⁸ Sr, ⁹⁵ Mo, ¹¹¹ Cd, ¹¹⁵ In, ¹⁰⁷ Ag, ¹³⁶ Ba, ²⁰⁸ Pb
Plasma gas flow rate/ L min ⁻¹	15.0
Auxiliar gas flow rate/ L min ⁻¹	0.9

Table 2. integrated ionic intensities and confidence intervals obtained for five droplets following the dried droplet calibration methodology.

Nuclide	Mean integrated intensity (counts)	RSD (%)
^{51}V	1979000	8.8
^{52}Cr	2455900	13
^{63}Cu	4644	14.8
^{208}Pb	11196000	10

Table 3. Integrated ionic intensities ($\times 10^{-3}$) for consecutive rasters performed on particular areas of solid residue and the clean sample.*

^{51}V				
	1 st raster	2 nd raster	3 rd raster	4 th raster
I_i solid residue	994 $\pm$ 87	83 $\pm$ 7	55 $\pm$ 5	47 $\pm$ 4
I_i clean sample	72 $\pm$ 6	33 $\pm$ 3	29 $\pm$ 3	28 $\pm$ 2
Net I_i defined as: I_i solid residue - I_i clean sample	922	50	26	19
% I_i with respect to the 1 st raster	100	5.4	2.8	2.1
^{208}Pb				
I_i solid residue	6546 $\pm$ 661	514 $\pm$ 52	239 $\pm$ 24	197 $\pm$ 20
I_i clean sample	331 $\pm$ 33	64 $\pm$ 6	56 $\pm$ 6	55 $\pm$ 5
Net I_i defined as: I_i solid residue - I_i clean sample	6215	450	183	142
% I_i with respect to the 1 st raster	100	7.2	3.0	2.3
^{63}Cu				
I_i solid residue	1921 $\pm$ 284	177 $\pm$ 26	110 $\pm$ 16	107 $\pm$ 156
I_i clean sample	156 $\pm$ 23	69 $\pm$ 10	69 $\pm$ 10	66 $\pm$ 10
Net I_i defined as: I_i solid residue - I_i clean sample	1765	108	41	41
% I_i with respect to the 1 st raster	100	6.1	2.3	2.3
^{52}Cr				
I_i solid residue	1213 $\pm$ 159	152 $\pm$ 20	65 $\pm$ 9	54 $\pm$ 7
I_i clean sample	93 $\pm$ 12	35 $\pm$ 4	35 $\pm$ 5	37 $\pm$ 5
Net I_i defined as: I_i solid residue - I_i clean sample	1120	117	30	17

% I _i with respect to the 1 st raster	100	10.5	2.7	1.5
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* See Table 1 for operating conditions

Table 4. Comparison of the concentrations obtained by applying the new calibration method against those for a glass certified reference material.[#]

Element	Determined concentration 1 ($\mu\text{g g}^{-1}$)*	Determined concentration 2 ($\mu\text{g g}^{-1}$)*	Certified concentration ($\mu\text{g g}^{-1}$)
Ni	42 $\pm$ 6	44 $\pm$ 6	38.8 $\pm$ 0.2
Sr	82 $\pm$ 12	82 $\pm$ 11	78.4 $\pm$ 0.2
Pb	40 $\pm$ 6	35 $\pm$ 5	38.57 $\pm$ 0.2
Ag	23 $\pm$ 3	21 $\pm$ 3	22.0 $\pm$ 0.3
Mn	51 $\pm$ 8	47 $\pm$ 7	39.6 $\pm$ 0.8
Cu	39 $\pm$ 6	35 $\pm$ 5	37.7 $\pm$ 0.9
Co	46 $\pm$ 7	ND	35.5 $\pm$ 1.2

[#] See Table 1 for operating conditions

*The confidence intervals corresponded to $\pm \frac{t s}{\sqrt{n}}$ where n = 5.

Table 5. Elemental concentrations (mg Kg^{-1}) encountered by applying the new calibration method and an acid microwave digestion procedure.

Element	Alumina based catalyst		Alumina based catalyst		Zeolite	
	1		2			
	DDCA	MW	DDCA	MW	DDCA	MW
Ni	11.4 ± 1.9	8.6 ± 1.3	7.9 ± 0.2	6.04 ± 0.05	5.1 ± 0.6	5.02 ± 0.17
Pb	0.96 ± 0.16	1.1 ± 0.3	X	X		
Cu	3.7 ± 0.6	2.6 ± 0.2	7.0 ± 1.0	7.1 ± 0.9	X	X
Co	X	X	3.0 ± 0.4	3.8 ± 0.6	1.2 ± 0.2	1.21 ± 0.11
V	4.3 ± 0.7	4 ± 2	0.9 ± 0.2	0.6 ± 0.2	1.8 ± 0.2	2.15 ± 0.14
Cr	4.1 ± 0.7	3.3 ± 1.3	5.4 ± 0.8	4.6 ± 0.8	6.5 ± 0.8	9.4 ± 0.2
Ba	0.44 ± 0.07	0.41 ± 0.19	X	X	0.67 ± 0.08	0.76 ± 0.05
Fe	54 ± 9	52 ± 6	25 ± 4	30 ± 3		
Mo	X	X	1.8 ± 0.3	2.0 ± 0.7		
Mn					2.0 ± 0.2	1.89 ± 0.09

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Figure 1. Scheme of the strategy followed in the present work.

Figure 2. ^{51}V Calibration lines obtained on an alumina based hydrotreatment catalyst using three different approaches in order to ablate the droplets.

Figure 3. Integrated signals corresponding to the four rasters performed on the area where the droplet was initially deposited (grey bars) and on the area without droplet (black bars). Operating conditions are included in Table 1. (a) ^{51}V ; (b) ^{208}Pb .

Figure 4. SEM images corresponding to the craters generated on the surface of (a) the alumina-based catalyst 1, (b) lithium tetraborate and (c) the spent zeolite. Laser beam diameter: 100 μm ; pulse frequency: 20 Hz; laser shots: 20; pulse energy: 2.7 mJ (60%).

Figure 5. Integrated signals obtained for four different samples. Operating conditions as indicated in Table 1.

Figure 6. Calibration line obtained for ^{60}Ni by applying the dried droplet calibration methodology to the analysis of alumina based catalyst 1.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Liquid standards are deposited, dried and ablated from the solid sample surface for accurate analysis through Laser Ablation ICP-MS