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Simultaneous determination of V, Ni, Ga and Fe in fuel fly ash using solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry.

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Abstract

A green and simple method has been proposed in this work for the simultaneous determination of V, Ni, Ga and Fe in fuel ash samples by solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry (SS HR CS GFAAS). The application of fast programs in combination with direct solid sampling allows eliminating pretreatment steps, involving minimal manipulation of sample. Iridium treated platforms were applied throughout the present study, enabling the use of aqueous standards for calibration. Correlation coefficients for the calibration curves were typically better than 0.9931. The concentrations found in the fuel ash samples analyzed ranged from 0.66 to 4.2 % for V, 0.23 to 0.7 % for Ni, 0 to 5.4 mg/Kg for Ga and 0.10 to 0.60 % for Fe. Precision (%RSD) were 5.2, 10.0, 20.0 and 9.8% for V, Ni, Ga and Fe, respectively, obtained as the average of the %RSD of six replicates of each fuel ash sample.

The optimum conditions established were applied to the determination of the target analytes in fuel ash samples. In order to test the accuracy and applicability of the proposed method in the analysis of samples, five ash samples from the combustion of fuel in power stations, were analysed. The method accuracy was evaluated by comparing the results obtained using the proposed method with the results obtained by ICP OES previous acid digestion. The results showed good agreement between them.

1. Introduction

The on-going economic growth coupled with the increasing standards of living has made us rely heavily on energy in our lives, especially after the Industrial Revolution in the last few centuries [1]. Energy is typically generated from the combustion of fossil fuels in various sectors including agricultural, transportation and industrial sectors. Diesel is highly consumed to generate electricity in Power Stations. The complete combustion of heavy fuel or diesel is not possible and the incomplete combustion will come out with mixture of substances known as fly ash [2,3]. These ashes may contain heavy metals as part of the natural composition of the fuel and/or inorganic material that was added through the refining process [4]. For example, the content of Molybdenum in some diesel samples comes from the use of molybdenum oxide in the oxidative desulphuration of diesel fuels [5]. Other metals such as nickel, vanadium or manganese may have both a natural or artificial origin [6]. If these ashes are not properly disposed of, they become environmental problems, such as dusting, leakage of acid liquids, and pollution with heavy metals. The research on this topic indicated that fly ash produced in heavy fuel power stations is rich in Ni, V, Fe, Mo, Mg, Na and C and among these metals Ni and V are the most valuable. Accordingly, fly ash would be a source of pollution due to metal leaching and in the same time it is commercially attractive due to the presence of high levels of V and Ni [3].

Thus, it is important to characterize fuel and its ashes. Different analytical techniques could be employed for the monitoring of trace elements in fly ash: inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and wavelength-dispersive X-ray fluorescence (WDXRF).

GFAAS is frequently used to determine trace elements due to its simplicity, low limits of detection and its extremely high tolerance for complex matrices. This potential has been further enhanced with the arrival of high-resolution continuum source (HR CS) GFAAS, in particular when aiming at the direct analysis of complex samples. The main advantages of HR CS GFAAS can be summarized as follows [7]: this technique allows the introduction of solid samples directly into the atomizer, eliminating the sample preparation procedure, which is time consuming, requires the use of hazardous acids and results in a significant dilution of the samples, and hence a decrease in the analyte concentration [8], it often makes possible the use of aqueous standard solutions for calibration [9]; the array detector permits the simultaneous monitoring of two hundred "wavelength sectors" (pixels), enabling efficient correction for many unwanted spectroscopically events. This aspect, in combination with the higher radiation intensity of the Xe (only one lamp source is needed) makes it feasible to obtain better-defined signals at lower

analyte levels, which means, better limits of detections, on the other hand, it is possible to decrease the sensitivity and therefore expand the working range to majority elements by measuring the absorbance at the wings of absorption lines [10,11], the technique still offers a considerably superior approach for the mathematical correction of complex, high and even rapidly changing backgrounds, since they are monitored simultaneously with the atomic absorption lines [12-16]; non-metals, such as Cl, F, P or S, can be determined at relatively low levels, since the most sensitive atomic lines for these elements are situated in the far UV region, which is not accessible for line source AAS instrumentation [17, 18].

The employment of chemical modification has earned a place of privilege in GFAAS. Chemical modification has evolved from the classic matrix modifiers described by Ediger [19], towards the permanent modification introduced by Shuttler in 1992 [20]. Amongst the chemical modifiers, the noble metals of high melting point (Ir, Pd, Pt, Rh and Ru) and the carbide forming elements (Hf, Mo, Nb, Ta, Ti, V, W, Zr) are the most employed either as mono-compound modifiers or combined [21]. Particularly in the case of the platinum group modifiers, the study by Pedro et al [21] found that Ir showed the most homogeneous distribution on the graphite furnace. The most important advantages of permanent modifiers over conventional modifiers application include extended tube lifetime, lower reagent blank and detection limit [22]. Iridium was the permanent modifier employed in this work to solve some problems found concerned with tailing of the atomization curves of V and carbide formation. In the pre-atomization stage, thermal decomposition of vanadium compounds leads to formation *inter alia* of vanadium carbide, which results in reduction of sensitivity and reproducibility [23], else of memory effects. Carbide forming modifiers are not recommended because produced poor sensitivity and also increased the memory effect [24].

Given the above considerations, the present work describes the simultaneous determination of V, Ni, Ga and Fe in fuel fly ashes by SS HR CS GFAAS, employing Ir as permanent modifier. The goal was to develop a fast and simple methodology that permits the use of aqueous standards for straightforward calibration and the simultaneous determination of V, Ni and Fe, as majority elements and Ga as trace element.

To the best of the authors' knowledge, no report has made use of SS GFAAS to investigate the simultaneous determination of V, Ni, Ga, and Fe in solid samples. However, the use of SS GFAAS can be a very suitable analytical method for this purpose, due to the potential of this technique to the direct analysis of these samples with minimal previous preparation, showing sufficient sensitivity for small amounts of solid ash samples, in which the analytes may be found at high or low concentrations.

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2. Experimental

2.1. Instruments

All the experiments in this work were carried out using a HR CS AAS, ContrAA 700, commercially available from Analytik Jena AG (Jena, Germany) and equipped with both graphite furnace and flame atomizers. The optical system comprises a xenon short-arc lamp (GLE, Berlin, Germany) operating in "hot-spot" mode as the radiation source, a high-resolution double echelle monochromator (DEMON) and a linear CCD array detector with 588 pixels, 200 of which are used for analytical purposes (monitoring of the analytical signal and BG correction), while the rest are used for internal functions, such as correcting for fluctuations in the lamp intensity. The selected wavelengths for the analysis were 294.2357 nm for V (one of the less sensitive V atomic lines), the spectral bandwidth per pixel is 1.3 pm, 294.3912 nm for Ni, the spectral bandwidth per pixel is 1.4 pm, 294.364 nm for Ga, the spectral bandwidth per pixel is 100 pm and 294.2357 nm for Fe, the spectral bandwidth per pixel is 0.36 pm. More details on this type of instrumentation can be found elsewhere [25].

The CS HR GFAAS instrument is also equipped with a transversely heated graphite tube atomizer, pyrolytic graphite tubes for solid sampling (without dosing hole) and an automated solid sampling accessory (SSA 600), which incorporates a microbalance with a readability of 1 mg [9]. The samples were introduced using solid sampling graphite platforms.

2.2. Samples and standards

All solutions were prepared using ultrapure water with resistivity of 18.2 M Ω cm, which was obtained from a Milli-Q purification system (Bedford, MA, USA). The vanadium, gallium and nickel solutions were prepared daily by diluting commercially available 1000 mg L⁻¹ standards and iron solution was prepared daily by diluting commercially available 10000 mg L⁻¹ standard (Merck, Darmstadt, Germany). The solution of chemical modifier was prepared from the stock solutions 1000 mg L⁻¹ (Merck, Darmstadt, Germany).

A number of fuel ash samples provided from the University of Lincoln have been analysed in order to demonstrate the applicability of the developed method for real samples. These samples were also analysed by ICP OES previous acid digestion.

2.3. Procedure for solid sampling HR CS GFAAS analysis

All samples were directly analysed without any sample pretreatment, only a manual homogenization was performed for 2-3 min using a small agate mortar, immediately before analysis. The instrumental conditions and the temperature program used were carefully optimized and are summarized in Table 1. For the determination of V, Ni, Ga and Fe, external calibration was carried out simply against aqueous standard solutions; the calibration was performed by using the appropriate volumes of aqueous solutions of the specific concentrations, added with a micropipette onto the stamping platform. All the experiments were carried out in graphite platforms, preliminary treated with Ir as permanent modifier. The temperature program for the platform treatment with Ir is presented in Table 2. During each cycle 20 μl of 1000 mg L^{-1} were injected on the platform. The treatment was repeated 20 times to provide permanent quality of the Ir coating.

The solid sampling device used allows for automatic weighing and transport of the samples into the furnace. The empty platform was first transported to the microbalance using a pair of tweezers. After taring, an appropriate amount of sample (between 0.04 to 0.46 mg, depending on the sample) was placed on the platform and weighted. Finally, the platform was transferred into the graphite furnace and subsequently subjected to the temperature program. All these operations were fully controlled from a keyboard, except for the deposition of the sample and standards which was carried out manually. For each fuel ash analysis, six similar portions of sample were properly weighted. After that the samples were analysed, the average of the six measurements was taken as the representative value. In all cases, absorbance peak heights were selected as the measurement mode.

2.4. Dissolution and analysis of selected fuel ashes for comparison purposes

Approximately 100 mg of ash was accurately weighed into a beaker and mixed with 20 mL of 37% HCl and 20 mL of 68% HNO₃. The slurry was agitated using a magnetic stirrer and left boiling

for 24 hours. A watch glass was used to cover the beaker and minimise evaporation. Ultrapure water was also added as necessary to top up the solution volume losses from evaporation. After digestion the slurry was allowed to cool and insoluble solids were removed by gravity filtration through Whatman Number 3 filter paper. Filtrate was collected in a 200 mL volumetric flask. The filter paper was then washed in ultrapure water to displace any absorbed solution which was collected in the same volumetric flask. The filtrate was then made up to volume and analysed for metals with a Thermo Scientific ICP-OES 7000 using radial detection.

3. Results and discussion

3.1. Analytical context of the investigation. Direct determination of V, Ga, Ni and Fe in fuel ash samples.

The development of reliable analytical methods capable of the simultaneous quantitative determination of majority elements (V, Ni, Fe) and trace elements (Ga) in solid samples is challenging from an analytical point of view considerably increasing sample throughput (by eliminating the digestion and pre-concentration steps) while reducing the risk of contamination and/or losses.

The goal of this paper is to evaluate the use of solid sampling GFAAS for the direct analysis of V, Ni, Ga and Fe in fuel ash. Solid sampling CS HR GFAAS has rarely been used for the direct simultaneous determination of these elements and, to the best of our knowledge, there is no actual report on its performance for the analysis. It may offer a suitable performance, as discussed in the introduction, in particular taking into account the improvements introduced with the arrival of high-resolution continuum source technology.

3.2. Optimization of the working conditions for the analysis of the fuel ashes.

3.2.2. Wavelengths

One of the main characteristics of a HR CS GFAAS instrument is its excellent resolution, with a CCD detector comprising 588 pixels, of which 200 are used for analytical purposes while the rest are used for internal corrections. Each pixel monitors indicates a range of only 1 to 2 pm (the exact value depends on the wavelength: the lower the wavelength, the higher the resolution).

For the atomic line evaluated, the absorbance values obtained at each of three detector pixels (the central pixel plus the adjacent ones, $CP \pm 1$) were summed. First of all, suitable wavelengths need to be selected, the sensitivity of which must be adequate for the analyte content, as samples are not diluted. In principle, the aim of this work was the simultaneous determination of the most commercially attractive metals in fly ashes, V and Ni. The expected content of these analytes in these types of samples is high (from the analysis by ICP OES, previous dissolution, the content of these metals ranging from 0.21 to 4.53 % (w/w)), thus the use of secondary or, less sensitive lines seem to be recommended.

The use of CS HR GFAAS permits, with certain limitations, to determine several elements simultaneously. The simultaneous determination of several elements requires atomic lines in the same spectral window, which means, the atomic lines selected must be closely adjacent to be truly simultaneously monitored by the narrow spectral window of the detector (closer than 0.2 nm) [26, 27] and, moreover, these lines should show adequate sensitivity for all the target elements. Furthermore, when attempting a simultaneous determination the thermo-chemical behavior of the analytes in a graphite furnace (e.g., volatility and potential to interact with C) needs to be considered since, the more similar these are, the easier it will be to develop a simultaneous method [28-30].

The sensitivity of different atomic lines was evaluated through the analysis of a fuel ashes taken as model. Finally, the instrument detector was centered at 294.32 nm, a secondary line of V. Then, the wavelength of 294,3912 nm for Ni was chosen. Thus, the spectral range between 294.240 and 294.600 nm was observed. In this spectral range the measured fuel ash showed other peak at 294.364 nm assigned to Ga by the instrument software. Hence, Ga was included as other element to the simultaneous determination.

In this work some problems, mainly concerned with tailing of the V signal and carbide formation, were encountered as described by other authors [31-34]. In the pre-atomization stage, thermal decomposition of vanadium compounds leads to formation inter alia of vanadium carbides, which results in reduction of sensitivity and reproducibility. So, the use of different chemical modifiers as Triton X-100, Pd and high atomization temperatures were tested without good results. Amongst permanent chemical modifiers, Ir showed the most homogeneous distribution on the graphite furnace versus other platinum group modifiers [21]. On the other hand, carbide forming modifiers are not recommended because produced poor sensitivity and also increased the memory effect [24]. Then, graphite platforms were covered with Ir in order to avoid the contact between vanadium and graphite and to decrease the formation of vanadium carbides. The program used to cover graphite platforms with Ir was taken from the software of the instrument, showed in Table 2. Regarding, Ir has proved beneficial for V

determination, improving to some extent the pyrolysis temperature and producing thinner V peaks. However, the wavelength used for the determination of V was overlapped by an Ir line, due to this fact, other wavelength had to be chosen for V, 294.2357 nm. When this line was selected at principal line, the spectral range observed was from 294.1323 nm to 294.3912 nm, appearing another line at 294.2357 nm in the ash spectrum. This line was assigned to Fe by the software. So, it was possible simultaneously monitor resonance lines for four analytes, Fe, V, Ga and Ni. The established lines for the method were 294.2357 nm for V, 294.3912 nm Ni, 294.364 nm Ga, and 294.1323 nm Fe, (Figure 1). The pixel numbers during the determinations were established as the required sensitivity in the analysis by HR-CS GFAAS, as described by Heitmann et al. [10]. The expected content of these analytes in these types of samples is high above all vanadium, thus, for vanadium, one pixel was used, and to quantify Ni, Fe and Ga, the measurements were performed using three pixels.

3.2.3. Optimization of the experimental conditions for the pyrolysis and atomization steps

The establishment of a proper temperature program (pyrolysis and atomization steps) for the simultaneous measure of all involved elements is a crucial step. Generally, the pyrolysis temperature is determined by the most volatile element, and the atomization temperature is established considering the most refractory element [35]. For this purpose, pyrolysis and atomization curves were built up for each metal by using aqueous standard solutions of the analytes and one sample. The study of pyrolysis and atomization temperatures for each metal are shown in Figure 2 and 3, respectively, for 20 μL of a multi-element solution of 250 mg L^{-1} . The thermal behavior of the analytes was very similar both in samples and the aqueous standard solution. First, the atomization temperature was fixed at 2450 $^{\circ}\text{C}$, and the pyrolysis temperature was varied from 1000 to 1500 $^{\circ}\text{C}$. The results in Fig. 2 demonstrated a thermal stability for Ni in the entire studied range of temperature. In general, high pyrolysis temperature was achieved for Ga. Additionally, it was observed that the maximum allowed pyrolysis temperature for vanadium was 1350 $^{\circ}\text{C}$, after that significant losses of vanadium were observed above this temperature. Therefore, the pyrolysis temperature of the proposed method was established considering the thermal behavior of this element.

Afterwards, the atomization temperature was studied in the range of 2100–2550 $^{\circ}\text{C}$ at a pyrolysis temperature of 1350 $^{\circ}\text{C}$. The results in Fig. 3 show an increase in absorbance signals of vanadium and iron with the increase in atomization temperature. For gallium and nickel, the absorbance signals increased up to a temperature of 2200 and 2400 $^{\circ}\text{C}$, respectively, remaining

practically constant from these values. A posterior experiment was performed at 2650 °C, the maximum power heating of the graphite furnace, V and Fe signals improved while Ga signal decreased slightly and Ni signal remained constant. Finally, the atomization temperature of the method was selected to 2650 °C.

Once the pyrolysis and atomization temperatures were studied, and knowing that pyrolysis and atomization ramp steps are the most critical factors in order to remove most of the matrix components without analytes losses, and to obtain well defined atomization peaks for the solid samples, a surface response methodology (SRM) was used for the optimization of these steps. SRM is a useful way to adjust these variables in order to establish optimal measurement conditions. This includes a group of mathematical-statistical techniques that were designed to optimize the analytical response by producing a model in which a response function corresponds to several variables called factors. Three factors were optimized by following this methodology: pyrolysis and atomization ramps ($^{\circ}\text{C s}^{-1}$) and pyrolysis hold time (s). Multiple response (four response functions) rotatable uniform central composite designs were performed. The three factors CCD used in this investigation included a total of $2k+2k+n$ runs (16 experiments), where k is the number of studied factors, $2k$ are the points from the factorial experiments carried out at the corners of the cube (8 experiments) and $2k$ are the points carried out on the face centred star (6 experiments); n , number of experiments carried out at the centre of the experimental domain was fixed at 2. The repetition of the centred point was used to estimate the experimental error. The resulting 16 experiments were randomly performed. The lower and upper values given to the factors are given in Table 3. The experimental data were processed by using the STATGRAPHICS centurion program (version 16.1.11 for Windows) [36]. For the design, the significance of the effects was checked by analysis of the variance (ANOVA) and using p -value significance levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the p -value is less than 5% the effect of the corresponding factor is significant.

The estimated surface response for the multiple responses of all the elements is shown in Figures 4A and 4B. The data indicate that the interaction usually occurs between principal factors. This means that the response surface in the factorial space is curved in the domain of the experimental design. These figures show the combination of factors at which the optimum is reached. As a result of these observations, the optimal conditions for the multiple responses of the 4 target analytes obtained are shown in Table 4.

3.3. Performance of the method

Once the optima conditions were established for the measurement of the target elements by solid sampling HR CS GFAAS, the possibility of quantifying using calibration against aqueous standards was explored. The signal profiles obtained for aqueous and solid samples were quite similar, both provided complete atomization. However, it is hard to expect exactly the same mechanism to take place for a solid sample and for an aqueous solution, in order to eliminate the possible problems due to this fact, integrated peak areas were measured [37]. No carbonaceous residues were found in the platform after analysis. Ideally, if no matrix effects are detected, it is possible to construct the calibration curve with aqueous standard solutions when using SS HR CS GFAAS. The signals obtained for fuel ash samples were unimodal and well defined, and the 3D spectra showed no potential interferences (Figure 1).

The sensitivity of the analytical technique is high, and no problems could be determined regarding the minimum content of the target elements. As was commented in section 3.2.2., the pixel numbers during the determinations were established as the required sensitivity in the analysis, thus for vanadium, one pixel was used, and to quantify Ni, Fe and Ga, the measurements were performed using three pixels. In these conditions, the figures of merit for the sequential determination of V, Ni, Ga and Fe using HR CS GFAAS are presented in Table 5. The limits of detection (LOD) and quantification (LOQ) have been calculated as the concentration of analyte giving signal equivalent to three and ten times, respectively, the standard deviation of the blank signal plus the net blank intensity. Using the optimized conditions, this method enables the simultaneous determination of V, Ni, Fe and Ga using the external calibration technique, where the limits of detection and quantification are 24.13 ng and 47.53 ng for V, 1.20 ng and 2.23 ng for Ni, 9.0 pg and 15 pg for Ga, and 3.19 ng and 10.3 ng for Fe, respectively. The precision of the method was evaluated by examining the standard deviation of the concentrations obtained from all analyses of the solid samples for each type of material. The precision was expressed as the percentage of the relative standard deviation (RSD). The RSD values, obtained as the average of the %RSD of six replicates of each fuel ash sample, were 5.2, 10.0, 20.0 and 9.8% for V, Ni, Ga and Fe, respectively

3.4. Analytical applications

In order to test the accuracy and applicability of the proposed method in the analysis of samples, five fuel ash samples were analysed. The method accuracy was evaluated by comparing the results obtained using the proposed method with the results obtained from other analytical techniques. For this purpose, fuel ash samples were directly analysed by the proposed method and the results were compared with the results obtained digesting the samples of ashes and

subsequently analysed by inductively coupled plasma optical emission spectrometry (ICP OES) in Lincoln University laboratories. The obtained concentrations using the two methods show no significant difference at the 95% confidence level. These results are shown in Table 6.

A very good degree of agreement with the values was achieved in all cases. In fact, correlation coefficients obtained were very close to 1 in all cases. The corresponding paired t-tests were carried out to confirm that the differences observed were not statistically significant (the t values were 2.57 for V, 1.86 for Ni and 0.34 for Fe, while the critical value is 4.30).

4. Conclusions.

The developed method enables the simultaneous and direct solid determination of V, Ga, Ni and Fe in fuel ash samples SS HR CS GFAAS, in a simple and straightforward way, carrying out the calibration versus aqueous standards. Furthermore, it has to be pointed out that the application of Ir as modifier allows the simultaneous determination of the four target analytes even when the concentrations of V, Ni and Fe are higher than the Ga, using a single heating program for the proposed method. The obtained limits of quantification and detection were satisfactory for the simultaneous determination of the analytes in the analysed samples.

The feasibility of using calibration against solid standards, fast programs, Ir modifier and the minimum sample manipulation makes this procedure appropriate for routine applications. The analysis of ashes by SS HR CS GFAAS as the clear advantage of providing fast results, as no sample preparation at all is involved, beside the homogenization for the samples, avoiding the use of other reagents, which might be considered a contribution to the green chemistry. It might be expected that this purposed method could be extended to the determination of these elements in other kind of solid samples.

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Tables

Table 1. Temperature program adopted for the simultaneous determination of Vanadium,

Variable	Upper value	Lower value	Nickel, Gallium and
Pyrolysis Ramp /C s ⁻¹	500	50	Optima
Pyrolysis Time /s	60	10	Iron in fuel ash
Atomization Ramp /C s ⁻¹	3000	500	5
Atomization Time /s	80	5	HR CS GF
Pyrolysis Ramp /C s ⁻¹	500	50	AAS.
Pyrolysis Time /s	60	10	
Atomization Ramp /C s ⁻¹	3000	500	
Variable	Upper value	Lower value	
Pyrolysis Ramp /C s ⁻¹	500	50	
Stage Pyrolysis Temperature /°C	130	10	
Atomization Ramp /C s ⁻¹	3000	500	Max
Drying 1	130	30	Max
Drying 2	130	5	Max
Pyrolysis	1350	5	Max
Gas flow	1350	0	Min
Atomization	2650	3000	Min
Cleaning	2650	0	Max

Table 2. The temperature program for the platform treatment with Ir

Stage	Temperature (°C)	Ramp (°C s ⁻¹)	Hold time (s)	Ar flow rate (L min ⁻¹)
Drying 1	130	6	40	Max
Drying 2	160	50	20	Max
Pyrolysis	1000	5	25	Max
Gas flow	1000	0	5	Max
Atomization	1400	50	5	Max
Atomization	2000	1000	5	Max

Table 3. The lower and upper values given to the factors of CCD.

Variable	Upper value	Lower value
Pyrolysis Ramp /C s ⁻¹	500	50
Pyrolysis Time /s	60	10
Atomization Ramp /C s ⁻¹	3000	500

Table 4. Optima conditions.

Table 5. Analytical performance.

	V	Ni	Ga	Fe
LOD /ng	24,13	1,20	9,0 (pg)	3,19
LOQ /ng	47,57	2,23	15,0 (pg)	10,3

Table 6. Comparison between the results obtained using the proposed method and others that needed digestion before analysis.

Sample	Direct analysis				Indirect Analysis			
	V % (w/w)	Ni% (w/w)	Ga ppm (mg/Kg)	Fe% (w/w)	V% (w/w)	Ni% (w/w)	Ga ppm (mg/Kg)	Fe% (w/w)
SA	4.3±1.0	0.7±0.3	5.4±1.0	0.60±0.07	4.53	0.79	--	0.65
Rab UK2	0.89±0.05	0.186±0.008	2.5±0.6	0.22±0.03	0.89	0.25	--	0.36
Rab UK3	0.66±0.05	0.30±0.01	0.0003±0.0001	0.13±0.02	0.68	0.21	--	0.15
RAb U2	0.71±0.06	0.25±0.02	0.00035±0.00002	0.095±0.02	0.83	0.33	--	0.19
Rab U1	0.74±0.06	0.23±0.03	0.00030±0.00006	0.26±0.09	0.82	0.29	--	0.25

Figures

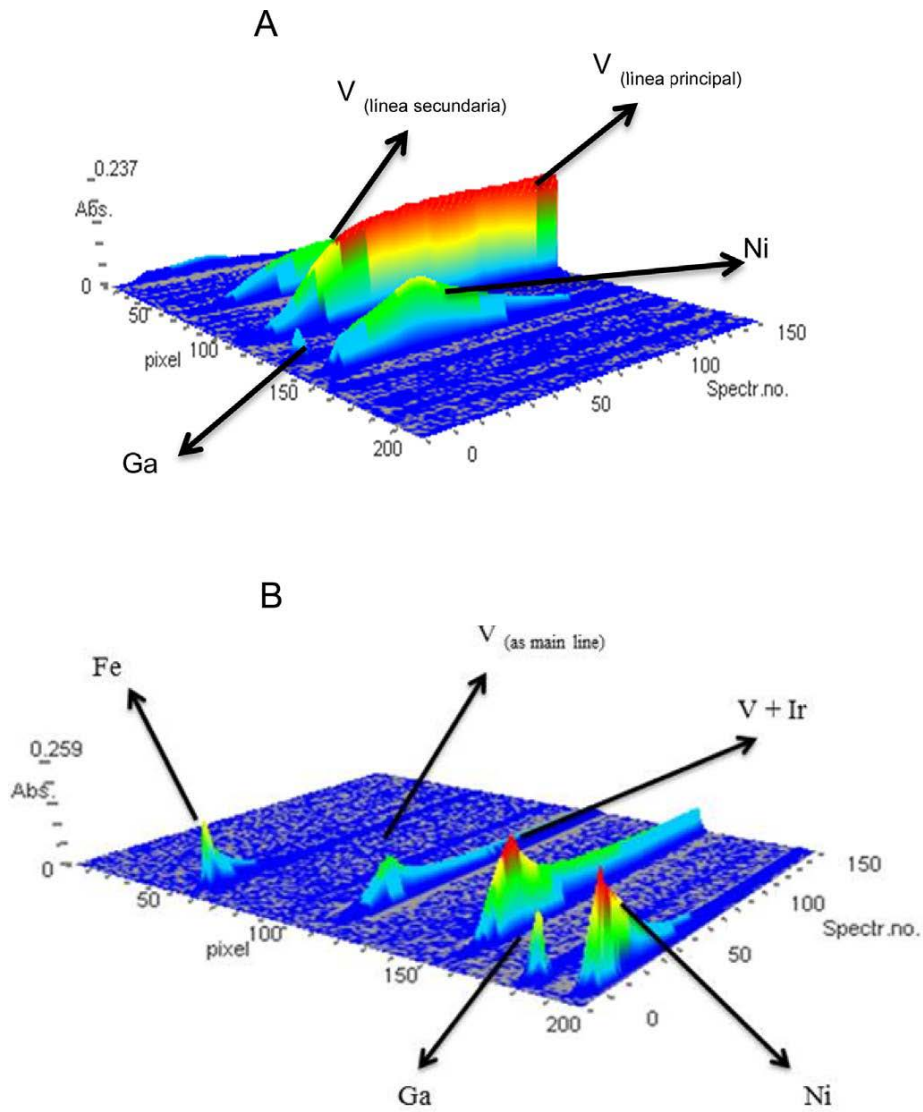


Figure 1. Time resolved absorbance spectra obtained upon SS HR CS GFAAS measurement for 5 μg Ga, Ni, V and Fe.

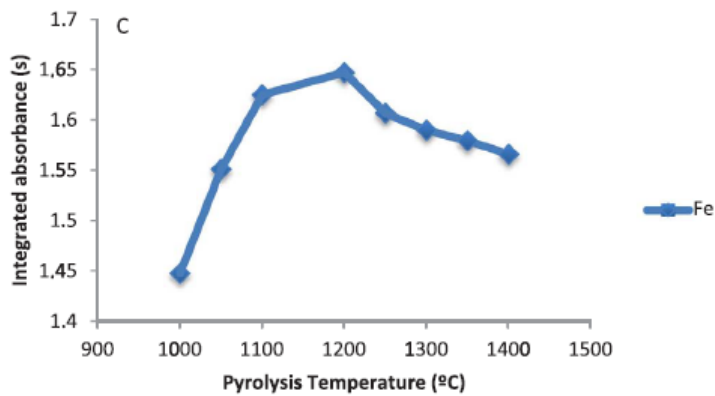
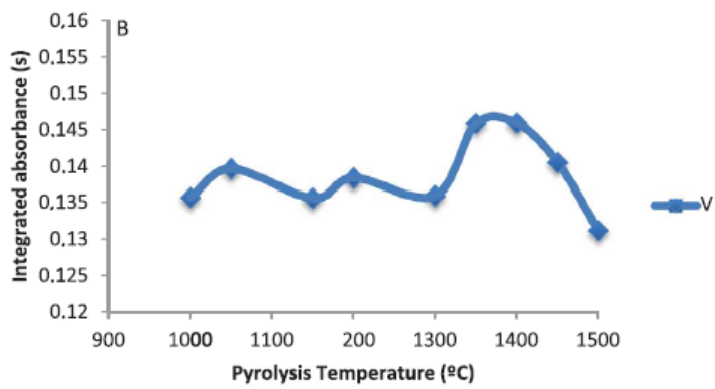
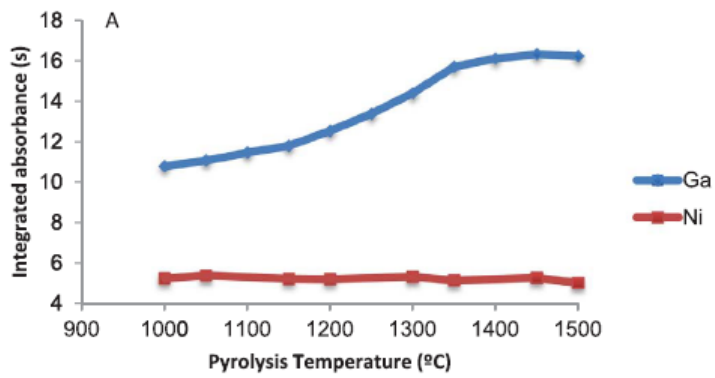


Figure 2. Pyrolysis temperature curves obtained for 5 µg Ga and Ni, V (B), Fe(C) in aqueous solution.

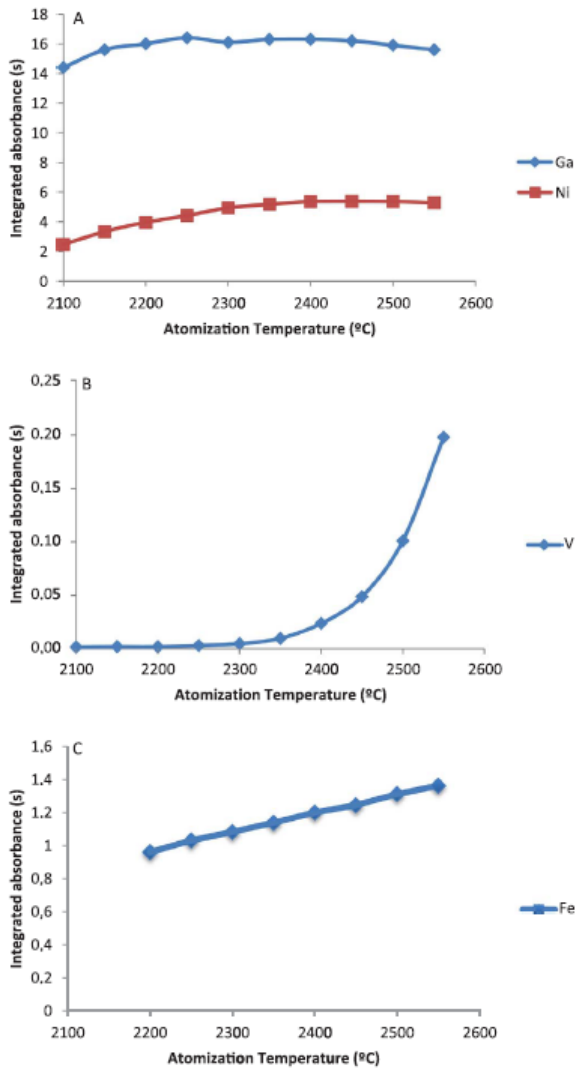


Figure 3. Atomization temperature curves obtained for 5 μg Ga and Ni, V (B), Fe(C) in aqueous solution.

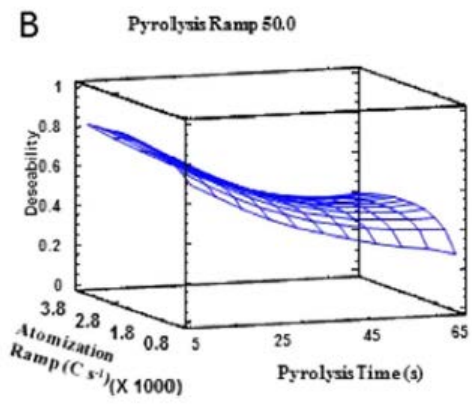
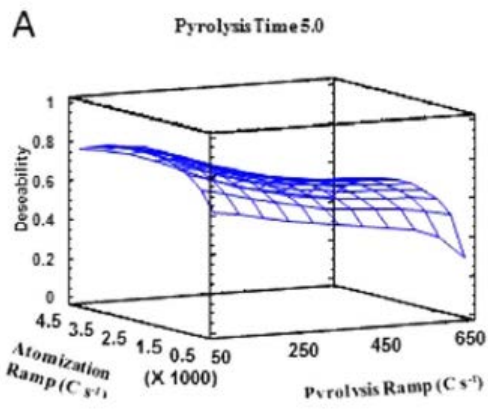


Figure 4. Results of the CCD design for pyrolysis and atomization ramps ($^{\circ}C s^{-1}$) and pyrolysis hold time (s).