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QUANTIFICATION OF CESIUM TRACES IN NATURAL SAMPLES BY FAES TECHNIQUE USING Pt-LOOP AS SAMPLE INTRODUCTION DEVICE INTO THE METHANE-AIR FLAME

ANDREEA-REBEKA ZSIGMOND[a,*], **LADISLAU KÉKEDY-NAGY**[b]

ABSTRACT. A rapid and simple FAES technique for the quantification of traces of cesium in natural samples is described. A volume of 3 μL of liquid sample was placed on a Pt-wire, dried, and atomized in the methane-air flame. The flame atomization conditions of cesium were optimized, which are as follows: λ = 852.19 nm, the height of 2 mm over the burner head, gas flow rates of 200 L h^{-1} air and 24 L h^{-1} methane. The effect of Na, K, Mg, Ca on the emission of cesium was studied too. Boric acid, citric acid and acetone were tested, as chemical modifiers. The lowest limit of quantification (6σ) obtained is of 11.9 ± 1.2 pg in the presence of 10 % v/v acetone ($P = 0.05$). The cesium content of mineralwater and lichen samples has been determined by using the standard addition method. The concentration of cesium varied between 0.016–0.124 mg.L^{-1} in the waters and 0.76–5.36 mg.L^{-1} in the lichens. The results of the two procedures agree within the determination errors.

Keywords: *flame, atomic emission, Pt-loop, cesium, water, lichen*

INTRODUCTION

Cesium is an alkaline metal; its compounds are in general chemically similar to those of other alkali elements. It resembles most with potassium and rubidium, the chemistry of cesium is more like that of these two elements than that of the lighter alkali ones. Cesium is the rarest of the naturally occurring alkali metals, being widely distributed in the earth's crust at very low concentrations. Granites contain in average 1 ppm cesium, sedimentary rocks 4 ppm, and seawater 0.2 ppm, respectively [1]. The presence of cesium in natural waters as a trace element provides main hydrogeological informations. Lichen is a widely used biomonitor for air pollution, which can easily accumulate different metals.

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[a] Sapientia Hungarian University of Transylvania, Faculty of Sciences and Arts, Str. Matei Corvin, No. 4, RO-400112, Cluj-Napoca, Romania, * *zsigmond.andrea@kv.sapientia.ro*

[b] Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Str. Arany János, No. 11, RO-400028 Cluj-Napoca, Romania

Analysis of trace levels is carried out by the most appropriate technique, which may include atomic emission and absorption spectrometry, X-ray fluorescence spectrometry etc. [2–5]. Cesium was quantified in natural waters by FAES technique using methane-air flame, the limit of detection being of 3 μg.L^{-1}[6]. For low levels of cesium in medical research, the proton induced X-ray emission technique has been developed [7]. Cesium has also been determined in porcine brain by instrumental neutron activation analysis [8]. The most sensitive, but most expensive technique for the cesium quantification is the ETV-ICP-MS, which has limit of detection of tenth of ng.L^{-1} [9].

Cesium ionizes significantly in hot media, as in acetylene flames or in ICP plasma, phenomenon which can be confined by use of an ionization suppressor. So, the cooler flames as, methane-air (M-A), PB-air etc. are advantageous for cesium assay. Using the electron avalanche amplification of the laser enhanced two-step ionization of Cs in hydrogen and propane flames proved to be very sensitive [10]. The sensitivity of the determinations could be further increased by sample atomization from an electrically heated platinum loop, investigated first for three decades by Berndt and Messerschmidt [11]. The main feature of this technique, by comparing with the direct nebulization, is the lower detection limit (about one order of magnitude) and considerably less sample volume necessity for the analysis (few microliters only). The use of low-temperature flame, including the M–A flame, in combination with platinum wire atomization is not reported, the cesium content was not quantified in this way.

The aim of this study is to elaborate and evaluate a sensitive micro-analytical technique for the rapid and simple quantification of traces of cesium from natural mineral water springs and digested lichen samples.

RESULTS AND DISCUSSION

Optimization of the operating conditions

First the observation height over the burner head (h) and the flame composition has been optimized. For this purpose 3 μL of 1 mg.L^{-1} Cs solution was atomized into the M-A flame, the burner head being moved downward in 1 mm steps in the 2 – 6 mm height domain. The results show that the intensity of the analytical signal decreases uniformly versus the height with the simultaneous increase of the standard deviations. The maximal value of the S/N was registered at h = 2 mm, so this value was considered as optimal.

Next the influence of the flame composition on the Cs analytical signal was studied, by using 6 different air- methane flow rates (L.h^{-1}): 200-22, 200-24, 300-34, 300-36, 400-44 and 400-46. In all cases stable flame was obtained. Five parallel measurements were made, the mean, the standard deviation, the S/N was calculated. The results are presented in the Fig.1.

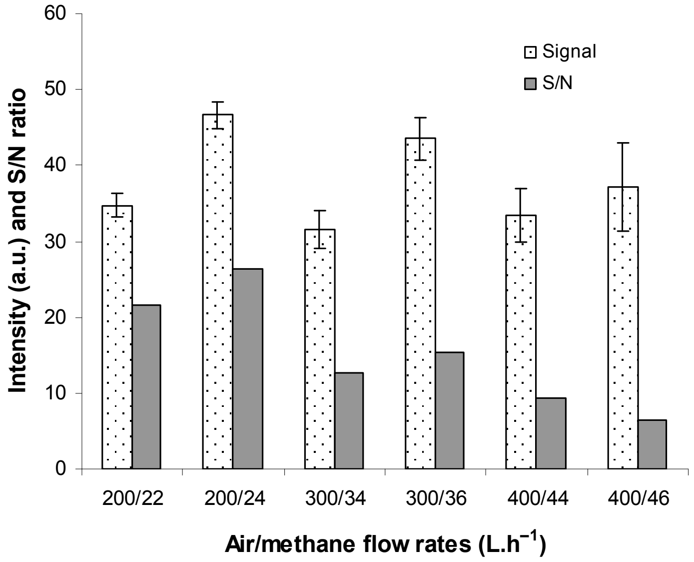


Figure 1. Influence of the air/methane flow rates on the analytical signal and the S/N ratio (Cs 1 $mg.L^{-1}$)

The increase of the air/methane flow rates lead to the decrease and the reproducibility of the analytical signal. The signal intensity is always higher in reducing flame, despite of the air flow rate. The optimum flow rates at which the highest S/N was recorded (26.5) are of 200/24 $L.h^{-1}$, considered as optimal for cesium assay.

In the following step the bandpass of the monochromator was optimized. The spectral bandpass (determined by its width of the slit) as well as the reproducibility of the determinations are simultaneously influenced, but not in the same extent. Therefore the optimal slit width for which the S/N ratio is the highest can be determined. The flame and instrumental parameters used were the optimal ones, determined earlier. The influence of the slit on signal intensity and S/N ratio was studied in the 100-1000 µm domain, in steps of 100 µm. The influence of the slit width (d) of the monochromator on the 1 $mg.L^{-1}$ cesium emission and the background signal is represented in the Fig. 2. The emission signal increases steeply (over 9 times) up to 500 µm then varies insignificantly. The background signal up to 500 µm slit width is close to zero, then increases sharply. The standard deviation of the means is homogeneous up to a width of 500 µm and then they differ significantly. The highest value for the S/N ratio was found at this value of the width of 500 µm, considered optimum.

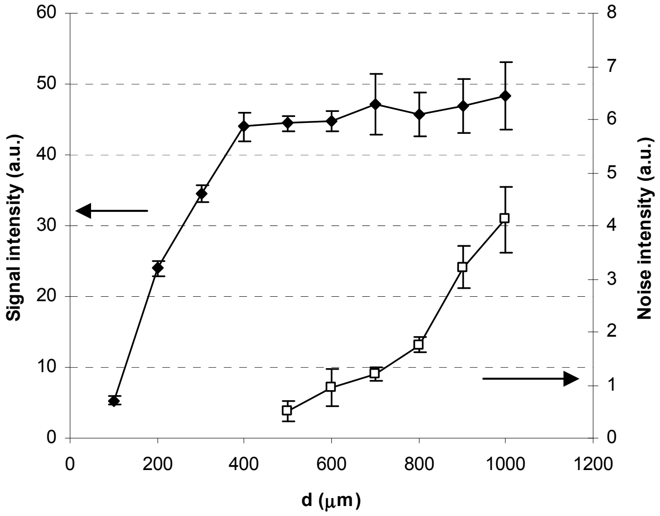


Figure 2. Influence of the slit width (d) of the monochromator on the 1 mg.L^{-1} cesium emission and the background signal

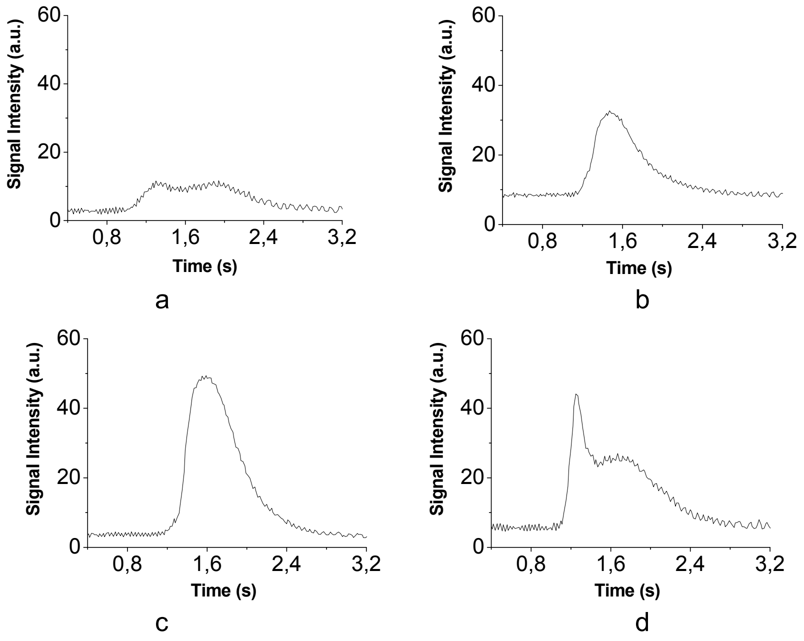
Study the influence of chemical modifiers

Three chemical modifiers have been tested: boric acid, citric acid and acetone. Boric acid is known as an oxide generating agent from inorganic chlorides [12]. At 600 °C it reacts with chlorides and evaporates as volatile BCl_3. The dissociation energy of the Cs_2O is considerably lower (297 kJ.mol^{-1}), than of the CsCl (439 kJ.mol^{-1}). It is expected, that the generation of Cs atoms in the flame should be facilitate by the cesium-oxide rather than by the cesium-chloride. The influence of the citric acid is not well known, although its benefic effects have already been proved [13]. The acetone is known to form complexes with alkali metals in aqueous solutions [14, 15], by yielding a low boiling point organic compound. The concentration of Cs standard in all cases was of 0.5 mg.L^{-1} to which boric and citric acid was added in final concentrations of 5, 10, 20, 50, 100, 200, 400, 800 mg.L^{-1} and 5, 10, 20, 50, 100, 200, 400, 500 mg.L^{-1}, respectively. Acetone was added in concentrations of 5, 10, 15 and 20 % (v/v). In all cases five replicate measurements were made, the mean peak height and peak area values have been calculated (Table 1). It was found; that all the chemical modifiers tested enhance the analytical signal, the most efficient proved to be the citric acid in a concentration of 100 mg.L^{-1}. The evaporation time of the compound from the platinum surface has been recorded too (Table 1). The cesium compounds evaporate in the shortest time when boric or citric acid is present. Presence of acetone shortens the evaporation time, but less outstanding.

Table 1. Influence of chemical modifiers on the emission signal of cesium

Solution	Peak height (a.u.)	Peak area (a.u.)	Relative signal enhancement		Evaporation time (s)
			Peak height	Peak area	
0.5 mg.L^{-1} Cs	12.47 ± 1.07	711.6 ± 61	1.0	1.0	2.11 ± 0.05
0.5 mg.L^{-1} Cs + 10 % (v/v) acetone	20.80 ± 0.46	1029 ± 72	1.7	1.4	1.96 ± 0.04
0.5 mg.L^{-1} Cs + 100 mg.L^{-1} boric acid	24.17 ± 0.60	851.8 ± 65	1.9	1.2	1.58 ± 0.02
0.5 mg.L^{-1} Cs + 100 mg.L^{-1} citric acid	48.93 ± 2.80	1709 ± 74	3.9	2.4	1.63 ± 0.03

In order to understand better the influence of the chemical modifiers, the change of the analytical signal versus time has been recorded too (Fig. 3). The shape of curve of the analytical signal for cesium alone shows two peaks, corresponding to different cesium compounds with different boiling points as well as dissociation energies. The first, the more volatile one, should be the oxide or hydroxide and the second one, with higher boiling point, should be the chloride (Fig. 3.*a*.). In the presence of 100 mg.L^{-1} boric acid the peak height increases, there appears a single peak, which is likely corresponding to the more volatile and easier dissociating cesium-oxide (Fig. 3.*b*.).



a b

c d

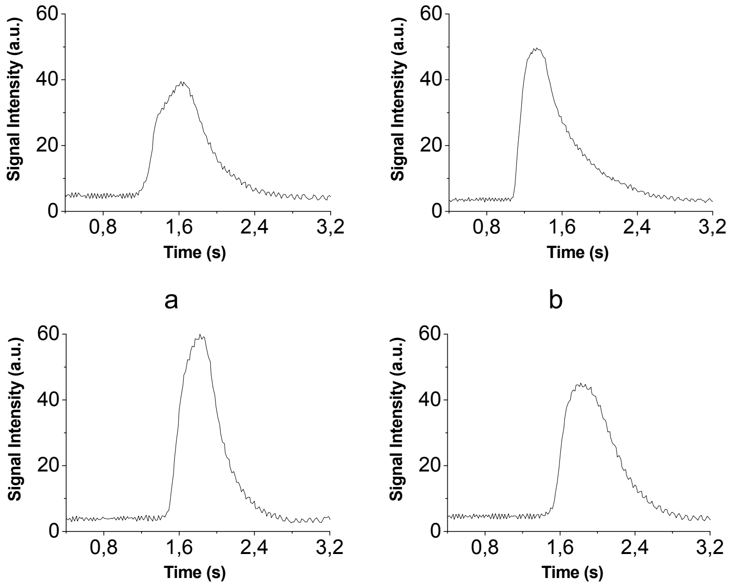
Figure 3. Variation of the emission signal of 0.5 mg.L^{-1} Cs versus time: alone (*a*) and in the presence of 100 mg.L^{-1} boric acid (*b*); 100 mg.L^{-1} citric acid (*c*); 10 % (v/v) acetone (*d*)

In the presence of 100 mg.L^{-1} citric acid the form of the analytical signal is similar to that obtained earlier, but the peak is higher presumably due to the complete dissociated Cs compound (Fig. 3.*c.*). In the presence of acetone the shape of the signal resembles the most with the signal of the cesium, with a more pronounced peak of the more volatile and easier dissociated compound (Fig. 3.*d.*). The higher signal peak and larger peak area suggests that acetone enhances the evaporation of cesium, and it generates the formation of the more volatile and easier dissociated cesium-oxide.

Study of the chemical interferences

The influence of Na, K, Mg and Ca on the emission signal of Cs has been studied. The metals have been added to the 0.5 mg.L^{-1} Cs solution in final concentrations of 5, 10, 20, 50, 100 and 200 mg.L^{-1}. Each element enhances the emission of Cs in low concentrations; magnesium is proved to be most efficient (it raises the peak height 4.8 times and the peak area value 3.6 times). Over 100 mg.L^{-1} of the interferent the analytical signal decreases in all cases due to the evaporation inhibition in solid phase.

The spectral interference which could have caused by the presence of K and Ca was tested too, be measuring the emission signal in the vicinity of the Cs line at λ = 849.0 nm. No emission signal was recorded, suggesting the absence of spectral interference.



a b

c d

Figure 4. Variation of the emission signal of 0.5 mg.L^{-1} Cs in the presence of: 50 mg.L^{-1} Na (*a*); 10 mg.L^{-1} K (*b*); 50 mg.L^{-1} Mg (*c*); 100 mg.L^{-1} Ca (*d*)

The change of the analytical signal vs. time in the presence of Na, K, Mg and Ca has been also recorded (Fig. 4.). In the presence of K, Mg and Ca the second peak disappears, or it is negligibly small comparing with the first one. The peak height increases considerably in the presence of K and Mg. Potassium acts as an ionization suppressor, magnesium-chloride is very likely to form a double salt with the analyte: cesium-carnallite during the heating process. The carnallite exhibits an incongruent melting below 200 °C [16]. In the presence of Na two overlapping peaks can be detected, the second peak being more pronounced.

Calibration results and figures of merit

The analytical figure of merit of the method was evaluated in the concentration range of 0.01-1 mg.L^{-1} at the optimized instrumental and atomization parameters. It was evaluated the limit of detection (LOD), precision and dynamic linear range of the method. In Table 2 there are listed the calibration data and limits of detection obtained in the presence of different matrixes.

Table 2. Calibration data and detection limits

Calibration conditions	Calculations	Sensitivity of the calibration	R factor	LOD (µg L^{-1})	LOD (pg)
CsCl	Peak height	39.37	0.9998	32 ± 14	67 ± 42
	Peak area	–	–	–	–
CsCl + 10% acetone	Peak height	307.6	0.9999	5 ± 2	14 ± 6
	Peak area	222.07	1.0000	4.0 ± 0.4	11.9 ± 1.2
CsCl + 100 mg.L^{-1} citric acid	Peak height	83.86	0.9995	10 ± 20	29 ± 47
	Peak area	348.2	0.9995	2 ± 28	7 ± 83
CsCl + 100 mg.L^{-1} boric acid	Peak height	44.81	0.9987	19 ± 65	56 ± 195
	Peak area	198.71	0.9995	4 ± 41	13 ± 123
CsCl + 50 mg.L^{-1} Mg	Peak height	62.05	0.9998	15 ± 19	44 ± 57
	Peak area	266.95	0.9999	3 ± 16	10 ± 48
CsCl + 10 mg.L^{-1} K	Peak height*	97.11	1.0000	11 ± 8	33 ± 24
	Peak area*	290.08	0.9997	4 ± 19	11 ± 57

*calibration data obtained only in the 0.1–1.0 mg.L^{-1} domain

The results show that both the peak and peak area values vary proportional in the whole calibration range with the cesium concentration. Unfortunately calibration in the concentration range of 0.01–0.1 could not be performed due to the significant Cs content of the K standard solution. All matrixes enhance the emission signal, i.e. the sensitivity, in average about 2 times. The instability of the analytical signal increases disproportionately, so due to the high dispersion values most of the calculated LOD values are meaningless. The best chemical modifier proved to be acetone in 10 % (v/v) by increasing the calibration sensitivity nearly 8 times without the significant increase of the standard deviation (the highest S/N value recorded among all). However, in the followings, the determinations were carried out in the presence of acetone. A limit of detection calculated for this case (6σ at P = 0.05) based on peak area values is the lowest of all, being of 4.0 ± 0.4 $\mu g.L^{-1}$ Cs, 11.9 ± 1.2 pg Cs respectively.

Quantification of cesium

Cesium has been quantified in optimal instrumental conditions, established earlier. Acetone has been added to the samples in final concentration of 10 % (v/v). Standard addition method has been used; the cesium standard has been added to the sample solutions in three steps. The final concentrations of the standards were of 0.02, 0.04 and 0.06 $mg.L^{-1}$ in the case of water samples, and of 0.05, 0.1 and 0.15 $mg.L^{-1}$ in the case of lichen samples. The results are shown in Table 3 and Table 4.

Table 3. The Cs content ($\mu g.L^{-1}$) of the mineral waters

Water sample	Peak height	Peak area
1	84 ± 37	82 ± 44
2	33 ± 12	27 ± 20
3	16 ± 4	26 ± 3
4	31 ± 4	35 ± 15
5	180 ± 80	200 ± 40
6	63 ± 9	71 ± 27
7	250 ± 20	230 ± 20
8	20 ± 8	18 ± 1
9	290 ± 10	270 ± 90
10	124 ± 40	132 ± 13
11	41 ± 1	41 ± 1
12	27 ± 1	30 ± 6
13	25 ± 2	25 ± 4
14	27 ± 30	24 ± 16

Table 4. The Cs content (μg.g^{-1}) of the lichens

Lichen sample	Peak height	Peak area
1	1.28 ± 0.32	1.44 ± 0.16
2	3.08 ± 1.40	3.64 ± 0.44
4	0.76 ± 0.32	0.96 ± 0.04
4	0.96 ± 0.24	1.28 ± 0.24
5	1.40 ± 0.28	1.52 ± 0.28
6	1.12 ± 0.44	1.44 ± 0.44
7	5.36 ± 0.80	6.2 ± 0.04
8	0.88 ± 0.24	0.84 ± 0.04

CONCLUSIONS

The FAES method using a Pt-loop sample introducing device proved to be efficient, sensitive for the quantification of traces of cesium in spring waters and lichens. The calibration curve is linear in the concentration range of 0.01–1.0 mg/L in the presence of 10 % (v/v) acetone. The LOD obtained is of 11.9 ± 1.2 pg. Cs also in the presence of 10 % (v/v) acetone (P = 0.05). Acetone, boric- and citric acids are proved to be efficient chemical modifiers by enhancing the analytical signal 1,7-3,4 times. Na, K, Mg and Ca enhance the analytical signal too, the most efficient being K and Mg. For the assay of Cs in natural samples the standard addition method was applied, the peak height and peak area data were calculated. The results between the two methods agree within the error of determination.

EXPERIMENTAL SECTION

Chemicals

Stock solutions of Cs, Na, K, Ca, Mg, boric acid and citric acid were of 1000 mg.L^{-1}, prepared from CsCl (Merck, Darmstadt, Germany), NaCl, KCl (Reactivul, Bucureşti, Romania), $CaCO_3$, Mg (Specpure, Johnson Matthey Chemicals Limited, England), H_3BO_3, $C_6H_8O_7$ (Reactivul, Bucureşti, Romania), respectively. As matrix modifier acetone (Merck, Darmstadt, Germany) was used. The calibration solutions were obtained by diluting a given volume of stock solution with double distilled water. The diluted solutions were prepared just before measurements.

Sampling and sample handling

The mineral spring waters originating from Harghita County (Romania) were collected during the 2010 summer period in accordance with EPA prescriptions: collected in 500 mL PET bottles, conserved on the spot with 1 mL of conc. HNO_3 and kept at 4 °C. The lichen samples have been collected from the Hasmas Mountains. The samples have been dried in oven at 105 ºC and meshed; desegregated by acid digestion at atmospheric pressure using 5 mL concentrated HNO_3 and 5 mL H_2O_2. The solutions have been diluted with double distilled water to final volume of 50 mL.

Instrumentation

The measurements were carried out at the atomic line of $\lambda = 852.19$ nm using a single-beam HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrometer equipped with a HEATH EU-700 scanning monochromator, a HEATH EU-700-30 type photomultiplier module and a M12FC51 (NARVA, Germany) photomultiplier (–1000 V). The photomultiplier signal was fed via a homemade I/U converter and a data acquisition card (Decision–Computer International Co. Ltd., USA) into Pentium II PC (120 MHz, 32 Mb RAM) computer. The data were processed with a home written Q-basic software program language using the boxcar averaging method. The fuel gas was the 99% purity methane from pipes; the oxidant was compressed air. The original slot-type burner (for C_2H_2-air flame) was replaced with a similar, Mecker-type, developed for atomic absorption/emission measurements in the methane-air flame [17]. The burner was operated at three different airflow rates of 200, 300, 400 L h^{-1} and at corresponding methane rates of 24, 26; 34, 36; 44 and 46 L h^{-1}, respectively. In all cases stable premixed flame was obtained. The atomizer, consisted of an $\Phi = 0.08$ mm-diameter 50-mm-long Pt-wire with a 3-mm-diameter loop in the middle, was described in details elsewhere [18,19]. The solutions were injected onto the platinum surface using a 10 µL volume 701N type syringe for gas chromatography (Hamilton Bonaduz AG, Switzerland).

Procedure

Aliquots of 3 µL solution were injected onto the platinum wire. The sample was dried by electrical heating of the wire to 120 °C for about 40 s and then it was introduced into the flame by manual rotation of the Teflon head. During atomization, electric heating was maintained. The change of the emission signal versus time until it reaches the blank signal level was registered. Five replicate determinations were made in each case, i.e., the mean, the standard deviation, and S/N were calculated. The homogeneity of the means was tested by the F test at a significance level of 0.05. The width of the slit of the monochromator was 0.500 mm (spectral band pass of 0.05 nm). The peak height values and the area under the peak have been considered, using the OriginLab Corporation (Northampton, MA 01060, USA) software package (version 7.0220).

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