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1   **Application of disposable starch-based platforms for sample**

2   **introduction and determination of refractory elements using graphite**

3   **furnace atomic absorption spectrometry and direct solid sample**

4   **analysis**

5

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14 **Abstract**

15 This study describes a new approach for direct solid sample analysis using

16 thermoplastic starch (TPS) platforms for the determination of Mo and V by high-

17 resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS

18 GF AAS). The TPS platform was prepared from a mixture of commercial corn starch

19 (28% amylase and 72% amylopectin), with sorbitol as plasticizer in a 70/30 mass-based

20 ratio. Different parameters affecting the film composition, such as proportion and

21 plasticizer type, were evaluated taking into account the behavior in the graphite tube

22 when the TPS platform was subjected to the heating program. The new sample

23 introduction approach has been shown to increase the graphite tube lifetime

24 significantly due to a much less pronounced tailing of the absorbance signals of

25 elements such as Mo or V, which makes possible reducing atomization and cleaning

26 times, compared to the use of a conventional graphite platform. Memory effects were

27 significantly reduced using the starch-based platform, resulting in improved precision.

28 Detection limit and characteristic mass were determined as 25 pg and 7 pg for Mo, and

29 130 pg and 18 pg for V, respectively. The accuracy was confirmed by the analysis of a

30 series of certified reference materials, including bovine liver, beef liver, rice flour and

31 urban dust for Mo, and coal, urban dust, lichen and particulate matter for V,

32 respectively.

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36

1. Introduction

38   Elemental analysis using graphite furnace atomic absorption spectrometry (GF AAS)

39   involves well-established procedures, although handling and preparation of solid

40   samples for analysis are still regarded as critical stages of an analytical method. Usually,

41   solid samples are brought into solution using 'classical' procedures, which might

42   include dry ashing,[1] alkaline fusion[2,3] or oxidative acid digestion.[4-6] Despite the

43   favorable characteristics inherent to each of these procedures, several limitations are

44   also associated to the analytical task of bringing a solid sample into a solution, which

45   depends on the sample, the analytes and their concentrations. Systematic errors due to

46   contamination by reagents or lab ware, or losses by volatilization are amongst the most

47   frequent issues, and may directly affect the accuracy and precision of the analytical

48   results. In this context, analyte determination based on the direct analysis of solid

49   samples (SS), which minimizes processing of the samples, appears as an interesting

50   alternative.[7,8]

51   The direct determination of trace elements by SS-GF AAS usually involves the

52   analysis of a powdered sample with controlled particle size. The advantages of this

53   procedure include simplified pre-treatment of the sample, allowing a reduction of

54   preparation time and minimized risk of contamination or analyte loss due to reduced

55   reagent consumption and to the absence of thermal treatment of the samples, among

56   others.[7,9,10]

57   Application of direct SS analysis to the determination of refractory elements may

58   have restrictions, which are mostly associated with the low atomization efficiency due

59   to the relatively high mass of the SS platform and the resulting slower heating rate and

60   lower final temperature compared to that of the tube wall. Elements, such as

61   molybdenum and vanadium are very stable, so that high atomization temperatures are

62   required, which significantly reduce the lifetime of graphite tubes and platforms. The

63   atomization efficiency would be higher for atomization from the wall; however, direct

64   SS analysis requires the use of graphite platforms for sample weighing and

65   transportation to the graphite furnace.[11] These aspects lead to the idea of using a

66   platform made of a thermally degradable material, such as starch, which would serve

67   simply as a sample holder to allow sample insertion into the graphite tube.

68   Starch is the main component of many grains, roots and tubers, such as corn, potato,

69   etc. and is a heterogeneous polysaccharide consisting of two polymers, amylase and

70   amylopectin, in variable proportions.[12,13] Starch films tend to be inflexible and brittle,

71   but the addition of plasticizers, such as glycerol or sorbitol, leads to the formation of

72   thermoplastic starch (TPS), which has improved mechanical properties. These

73   polymeric films have acquired great importance, which is mostly due to the fact that

74   they might be used as a source of biodegradable materials, renewable sources, with

75   relatively low cost.[14]

76   The aim of this work was to develop and to evaluate a new concept for direct SS

77   introduction for GF AAS, consisting of the use of TPS as a "platform" for the

78   determination of Mo and V in solid samples. The results obtained using the new TPS

79   platforms were compared to those for conventional SS graphite platforms, and certified

80   reference materials (CRM) were analyzed to evaluate the accuracy and practical

81   applicability of the proposed technique.

82   **2. Experimental**

83   *2.1. Instrumentation*

84   All measurements were carried out using a contrAA 600 high-resolution continuum

85   source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a

86   transversely heated graphite tube atomizer. The instrument is equipped with a 300 W

87   xenon short-arc lamp, operating in a 'hot-spot' mode, as a continuous radiation source

88   from 189-900 nm; a high-resolution double monochromator, consisting of a prism pre-

89   monochromator, an echelle grating monochromator, and a charge-coupled device

90   (CCD) array detector, providing a spectral bandwidth per pixel of about 1.2 pm at 200

91   nm.

92   Pyrolytically coated graphite tubes without platform, but with a dosing hole

93   (Analytik Jena, Part No. 407-A81.011), were used in all experiments with aqueous

94   standards and direct SS analysis. The solid samples were weighed directly onto SS

95   platforms (Analytik Jena Part No. 407-152.023) or TPS films using an M2P

96   microbalance (Sartorius, Göttingen, Germany). A manual solid sampling system, SSA 6

97   (Analytik Jena), was used to transport and insert the SS platforms or TPS films into the

98   graphite tube. Argon 99.996% (Oxilar, Florianópolis, Brazil) was used as purge and

99   protective gas. The temperature program used for Mo and V determination is shown in

100   Table 1.

101   A T1440 ultrasonic bath (Unique, São Paulo, Brazil), operated at 40 kHz and 81 W,

102   was used for preparation of the TPS polymeric films.

103   *2.2. Reagents and reference materials*

104   Ultrapure water obtained from a Mega ROUP Mega purity system (Equisul, Pelotas,

105   Brazil) with a specific resistivity of 18 MΩ cm was used throughout for preparation of

106   calibration solutions. The aqueous standards were prepared by serial dilution of the

107   individual stock standard solutions of 1000 mg L^{-1} Mo and V (Sigma-Aldrich,

108 Steinheim, Germany). Commercial corn starch (Maizena, Garanhuns, Pernambuco,

109 Brazil), sorbitol 99% (Vetec, Rio de Janeiro, Brazil) and glycerin (glycerol) 99.5%

110 (Vetec), were used as supplied to produce the polymeric films.

111 The certified references materials (CRM) NIST 1649a "Urban Dust", NIST 1577b

112 "Bovine Liver", NIST 1568a "Rice flour" (National Institute of Standards and

113 Technology, Gaithersburg, MD, USA) and NCS ZC 71001 "Beef Liver" (NCS, Beijing,

114 China) were used to verify the accuracy for Mo, and that of V was verified using BCR

115 No. 180 "Gas Coal" (Community Bureau of Reference, Brussels, Belgium), IAEA-336

116 "Lichen" (International Atomic Energy Agency, Vienna, Austria), NIST 1648a "Urban

117 Particulate Matter" and NIST 1649a "Urban Dust".

118 *2.3. Preparation of TPS platforms*

119 Different starch and plasticizer proportions, as well as plasticizer types were studied

120 considering the TPS film characteristics according to its behavior during the heating

121 program. Plasticizers are added to improve the mechanical properties such as

122 malleability of the polymeric film, and must be compatible with the biopolymer.[14]

123 Glycerol and sorbitol are amongst the most suitable plasticizers for starch, and glycerol

124 usually provides more pronounced effects upon the malleability of starch-based

125 films.[14,15] When produced in the laboratory, the starch is dispersed in water, a plasticizer

126 is added, and the ingredients are thoroughly mixed. During drying, the ingredients form

127 a uniform layer that gives rise to films.[16]

128 For preparation of TPS films, 0.5 or 1.0 g of starch were added into a 50 mL beaker,

129 followed by 15 mL of distilled water and 0.1 or 0.3 g of the plasticizer, which was

130 added to prevent the film from becoming brittle. The mixture was immersed in an

131 ultrasonic bath for 6 min in order to increase the homogeneity, and then kept under

132   magnetic stirring and heating to 55 °C for 35 min. Finally, the mixture was transferred

133   to a previously heated Petri dish and left to stand in a fume hood until complete

134   evaporation of the water. Afterwards, the TPS films were cut into fragments of 4 mm x

135   10 mm with stainless steel scissors, in order to acquire dimensions similar to a

136   conventional SS platform. The starch and plasticizer proportions were varied according

137   to the conditions shown in Table 2.

138   *2.4. Mo and V determination by HR-CS SS-GF AAS using TPS platforms*

139   Aliquots varying from 0.05 to 0.8 mg of each CRM were weighed on TPS or

140   graphite platforms and transferred to the graphite tube using the SSA 6 accessory. The

141   transfer of the two types of platforms is shown in Figs. 1A and 1B, and the position of

142   the TPS platform inside the graphite tube in Figs. 1C and 1D. The TPS platform is

143   disintegrating during the first pyrolysis stage of the temperature program shown in

144   Table 1, leaving the sample directly on the tube wall. The main resonance lines at

145   313.259 nm for Mo and 318.398 nm for V were used, and the integrated absorbance

146   summated over three pixels around the line core ($A_{\Sigma3,int}$) was used for signal evaluation.

147   Aqueous standard solutions were used for calibration for both elements, and calibration

148   solutions were pipetted directly onto the graphite tube wall in 20 µL aliquots.

149   **3. Results and Discussion**

150   *3.1 Evaluation of the TPS platforms*

151   A polymeric film made from a biopolymer is for the first time reported in this work

152   as a replacement material for the graphite platforms used in SS-GF AAS. One of the

153   main advantages associated to the use of a polymeric platform for refractory elements

154   resides in the fact that the platform readily decomposes in the pyrolysis stage, leaving

155   the solid sample in direct contact with the graphite tube wall. Under these conditions,

156   the temperature to which the analyte is subject is significantly higher than the actual

157   temperature of a graphite platform under the same nominal temperature,[17] leading to

158   enhanced atomization efficiency for refractory elements.

159   Actually, the dynamic and static (final) temperatures of tube wall and platform

160   during an atomization cycle were only measured accurately for a transversely heated

161   graphite tube with integrated platform;[17] however the results allow some extrapolation

162   also for a SS platform, which has a significantly greater mass. The graphite tube wall

163   was shown to heat very rapidly with some "overshooting" over the set temperature

164   when high heating rates are applied.[17] This effect might be very beneficial when

165   refractory elements are atomized from the tube wall. Platforms don't show this effect, as

166   they are heated by radiation from the tube wall, which causes a delay in the onset of

167   heating and a somewhat lower final temperature, the magnitude of both depends on the

168   mass of the platform used. This "platform effect" is beneficial for the determination of

169   volatile elements, and an essential part of the STPF concept.[18] For the most refractory

170   elements, however, this effect results in increased tailing of the absorption signal and

171   memory effects.

172   Ideally, the TPS film should be easy to manipulate, so that it can be cut into the

173   desired platform-like shape, and it should be sufficiently resistant to allow grapping by

174   the pair of tweezers used to insert the platform into the graphite furnace. Considering

175   these aspects, TPS films produced using a Petri dish with a diameter of 9 cm formed

176   from 1.0 g of starch and 0.3 g sorbitol were selected for further experiments.

177   *3.2 Optimization of temperature program for degradation of the TPS platforms*

178   The thermal degradation of TPS film platforms was evaluated during the drying and

179   first pyrolysis stage by inserting a small mass of film (about 0.02 mg) into the graphite

180   tube and monitoring its disintegration with the internal camera available in the contrAA

181   instrument. Complete degradation of the film was observed at temperatures above 500

182   ºC, within 20 s. Adoption of this 'pre-pyrolysis' stage led to a smooth disintegration of

183   the film, resulting in deposition of the solid sample directly onto the inner graphite tube

184   wall.

185   *3.3. Temperature program optimization for aqueous solutions and solid samples*

186   Molybdenum and V are thermally highly stable elements, which eliminates the need

187   to carry out individual optimization of pyrolysis temperatures for CRM and aqueous

188   solutions. Pyrolysis temperatures were selected based on previously published

189   procedures aiming at Mo and V determination available in the current literature,[19,20] and

190   set as 1200 °C and 1100 °C for Mo and V, respectively.

191   Fig. 2 shows the atomization curves for Mo and V in aqueous solution; the highest

192   sensitivity was found using 2650 °C for Mo and 2600 °C for V, respectively; however,

193   in the case of Mo the optimum atomization temperature might even be higher than 2650

194   °C, but this is the maximum temperature that can be selected in the equipment used in

195   this work.

196   In the same way, the behavior of Mo and V was evaluated using a solid CRM

197   weighed onto a TPS platform. The corresponding atomization curves are shown in Figs.

198   3A and 3B. Approximately 0.07 mg of NIST SRM 1649a (≈ 1.0 ng Mo) and around 0.7

199   mg of CRM IAEA 336 (≈ 1.0 ng V), were weighed onto TPS platforms and submitted

200   to the temperature program. The atomization curves for the aqueous standard solutions

201 and the solid CRM are very similar, with optimum atomization temperatures of 2650 °C

202 for Mo and 2600 °C for V, respectively.

203 In the case of V (Fig. 3B), the maximum sensitivity is obtained at 2600 °C, and in the

204 case of Mo the optimum atomization temperature is only slightly higher. These high

205 temperatures are due to the carbides and oxides of V and Mo which have high

206 stability.[11] The atomization temperatures selected for the next optimizations were 2650

207 °C for Mo and 2600 °C for V.

208 *3.4. Comparison between TPS film and conventional graphite platform*

209 The next step was to compare the behavior of Mo and V in direct contact with the

210 tube wall after introduction on a TPS film as a sample holder and a conventional SS

211 graphite platform. Approximately 0.07 mg of the CRM NIST 1649a ($\approx$ 1 ng Mo) was

212 weighed onto the TPS film and onto a graphite platform, respectively, using 15 s of hold

213 time for atomization in both cases. Fig. 4A shows the superimposed absorbance signals

214 for the two platform types, while Figs. 4B and 4C show the time-resolved absorbance

215 spectra around the 313.259 nm Mo line. Obviously, a much longer atomization time

216 would have been required for the atomization signal to return to the baseline,

217 particularly in the case of the graphite platform; however, the maximum time that can

218 be used at a temperature of 2650 °C is 15 s. Nevertheless, due to the higher temperature

219 of the tube wall, compared to the platform surface,[17] Mo is atomized with greater

220 efficiency and with less tailing when introduced on the TPS platform.

221 There appears another strong absorption line within the spectral range covered by the

222 detector, which is due to Ni (313.410 nm). This is not a problem, as the two lines are

223 well separated due to the high resolution of the monochromator.

224   Similar results were found for V when the samples were introduced into the graphite

225   furnace on TPS film or on a conventional graphite platform (Figs. 5A, 5B and 5C).

226   Approximately 0.7 mg of CRM IAEA-336 ($\approx$ 1 ng V) was accurately weighed onto the

227   platforms, and an atomization (hold) time of 20 s at 2600 °C was used. Fig. 5A shows

228   that, when the TPS film is used for sample introduction, atomization starts after about 1

229   s, the signal reaches a maximum after about 4 s and returns almost to the baseline after

230   about 15 s. In contrast, when the conventional SS graphite platform is used, atomization

231   only starts after about 3 s, the maximum is reached after 5-6 s with a much lower

232   maximum absorbance, and the signal does not return to the baseline within the 20 s of

233   atomization time. This is an important fact, since, as in the case of Mo, the lifetime of

234   the tube can be increased using TPS film by reducing the atomization time. Another

235   important point is the repeatability of the analytical signal using the TPS film, which

236   was much better when compared to the conventional graphite platform. This can be

237   explained by the faster atomization of the analyte during the first seconds in case of the

238   TPS film, where the gas phase temperature is higher due the absence of a graphite

239   platform, and the less pronounced tailing.

240   As in the case of Mo, different absorption lines can be seen in Figs. 5B and 5C in the

241   vicinity of the main analytical line of V. Firstly, there are the two additional lines of the

242   vanadium triplet at 318.342 and 318.541 nm, and there is also a strong Fe absorption at

243   318.48 nm.

244   *3.5. Comparison of direct SS analysis using TPS film and aqueous standard solutions*

245   The great perspective of using direct SS analysis with GF AAS is the possibility of

246   using aqueous standard solutions for calibration. In order to check this possibility in the

247   present case, aqueous solutions with an analyte mass of 0.3 ng Mo and 1.3 ng V,

248 respectively, were injected directly into the graphite tube onto the tube wall.

249 Approximately the same analyte mass in the form of solid samples was introduced via

250 the TPS platform and submitted to the temperature program in Table 1. The results that

251 are presented in Figs. 6 and 7 show that essentially the same integrated absorbance was

252 obtained in the case of Mo and that the signals were practically identical in the case of

253 V, respectively, indicating that aqueous standard solutions could be used for calibration.

254

255 *3.6. Calibration and figures of merit*

256   In the proposed method, TPS film platforms were used for direct SS analysis for Mo

257 and V determination using aqueous standard solutions for calibration. The linear

258 working range was from 0.09 to 5 ng Mo and from 0.5 to 20 ng V, respectively, with a

259 linear correlation better than R = 0.998. The limit of detection (LoD) was calculated as

260 3 σ/S (n = 10), where σ is the standard deviation of 10 blank measurements and S is the

261 slope of the calibration curve. The LoD found for Mo and V using the proposed method

262 was 0.025 ng Mo and 0.13 ng V, respectively, while the characteristic mass, m_0, was 7

263 pg for Mo and 18 pg for V, respectively. The figures of merit are summarized in Table

264 3.

265   It was essentially impossible, particularly in the case of Mo, to calculate figures of

266 merit for the graphite platform for comparison. The rapid deterioration of the graphite

267 tube and platform did not allow making a series of measurements for statistical

268 evaluation of the data. Fig. 8 shows an example for that problem; a quantity of about

269 0.22 mg of NIST SRM 1649a "Urban dust" has been analyzed eight times in sequence,

270 in both cases starting with a new graphite tube. The graphite platform was new as well

271 at the beginning of the experiment, but used for all the eight atomization cycles. A new

272   TPS platform had obviously to be used for each of the atomizations. Fig. 8 shows the

273   atomization signals that were obtained for the eighth measurement for each of the

274   platforms, which should be compared with those shown in Fig. 4A. The latter ones are

275   the first shot with a new tube and a new platform, the only difference being the sample

276   mass, which was more than three times higher in Fig. 8. It is obvious that the

277   atomization signal with the TPS platform remained essentially the same, whereas the

278   one with the graphite platform underwent a significant change. Actually, the absorbance

279   signal with the latter one changed with each atomization cycle, making any quantitative

280   evaluation impossible. The results obtained with the graphite platform for V were

281   clearly better than those for Mo; however, those obtained with the TPS platform were

282   still much better, so that no quantitative comparison has been made.

283   *3.7. Determination of Mo and V in CRM by HR-CS SS-GF AAS using TPS film*

284   The results of the determination of Mo in four CRMs, NIST 1577b (bovine liver),

285   NCS ZC 71001 (beef liver), NIST 1568a (rice flour), and NIST 1649a (urban dust)

286   using HR-CS SS-GF AAS and TPS film for sample introduction are shown in Table 4.

287   The results of the determination of V in CRM BCR 180 (gas coal), NIST 1648a (urban

288   particulate matter) and NIST 1649a using the same technique are shown in Table 5.

289   In all determinations the found values were in agreement with the certified ones at a

290   95% confidence interval (student t-test, $p > 0.05$), with relative standard deviations

291   (RSD) better than 8%. This shows that HR-CS SS-GF AAS using the new approach of

292   sample introduction on a TPS film and calibration against aqueous standard solutions

293   can be used for this kind of analysis.

294   **4. Conclusions**

295   One of the most beneficial results of using a TPS film for direct SS introduction for

296   GF AAS was the lifetime of the graphite tubes, which increased very significantly

297   compared to the use of conventional graphite platforms. This is mostly due to the

298   reduced tailing of the absorbance signals, which directly results in a reduction of the

299   atomization time. This is an important point because it is directly related to the cost of

300   analysis. Another important point is that the RSDs found in all determinations were

301   very low for direct SS analysis, demonstrating the repeatability of analytical signals

302   even for complex samples, such as coal and biological materials. The possibility of

303   using aqueous standard solutions for calibration further enhances the attractiveness of

304   the approach. It might be expected that the use of starch platforms for direct SS-GF

305   AAS analysis could be extended to the determination of other refractory elements in the

306   future.

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352 Table 1. Temperature program adopted for Mo and V determination using HR-CS SS-

353 GF AAS.

Stage	Temperature / °C	Ramp / °C s^{-1}	Hold / s	Ar gas flow-rate / L min^{-1}
Drying 1	110	6	15	0.3
Drying 2	160	5	15	0.3
Pyrolysis 1	510	10	20	0.3
Pyrolysis 2	1200[a]; 1100[b]	50	10	2.0
Atomization	2650[a]; 2600[b]	FP[c]	15[a]; 20[b]	0
Cleaning	2650	0[a]; 150[b]	4	2.0

354 [a] molybdenum [b] vanadium [c] FP = Full power

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356

357 Table 2. Combined conditions adopted to evaluate the characteristics of the TPS film

358 used for HR-CS SS-GF AAS analysis.

Experiment	Starch mass / g	Plasticizer type	Plasticizer mass / g	Petri dish diameter / cm
1	1.0	sorbitol	0.3	7.5
2	1.0	sorbitol	0.3	9.5
3	0.5	sorbitol	0.1	9.5
4	0.5	glycerol	0.1	9.5
5	1.0	sorbitol	0.1	9.5

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361 Table 3. Figures of merit for the determination of Mo and V using HR-CS SS-GF AAS

362 and TPS film for direct SS analysis with calibration against aqueous standards.

Parameters	Mo	V
Limit of detection, pg	25	130
Characteristic mass, pg	7	18
Correlation coefficient, R	0.999	0.998
Linear working range, ng	0.09 - 0.50	0.5 - 20

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366 Table 4. Molybdenum determination in different CRMs by HR-CS SS-GF AAS with

367 TPS film for SS introduction and aqueous standard solutions for calibration. The values

368 represent the mean of three measurements ± SD.

CRM	Found / $\mu g\ g^{-1}$	Certified / $\mu g\ g^{-1}$	RSD / %
NIST 1577b	3.6 ± 0.1	3.5 ± 0.3	3
NIST 1568a	1.6 ± 0.1	1.46 ± 0.08	6
NCS ZC 71001	3.5 ± 0.3	3.76 ± 0.3	8
NIST 1649a	13.9 ± 0.5	13.5 ± 0.9	3

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372   Table 5. Vanadium determination in different CRMs by HR-CS SS-GF AAS with TPS

373   film for SS introduction and aqueous standard solutions for calibration. The values

374   represent the mean of three measurements ± SD.

CRM	Found / μg g^{-1}	Certified / μg g^{-1}	RSD / %
NIST 1649a	336 ± 24	345 ± 13	7
NIST 1648a	132 ± 2	127 ± 11	1
BCR 180	21 ± 1	19 ± 1	7

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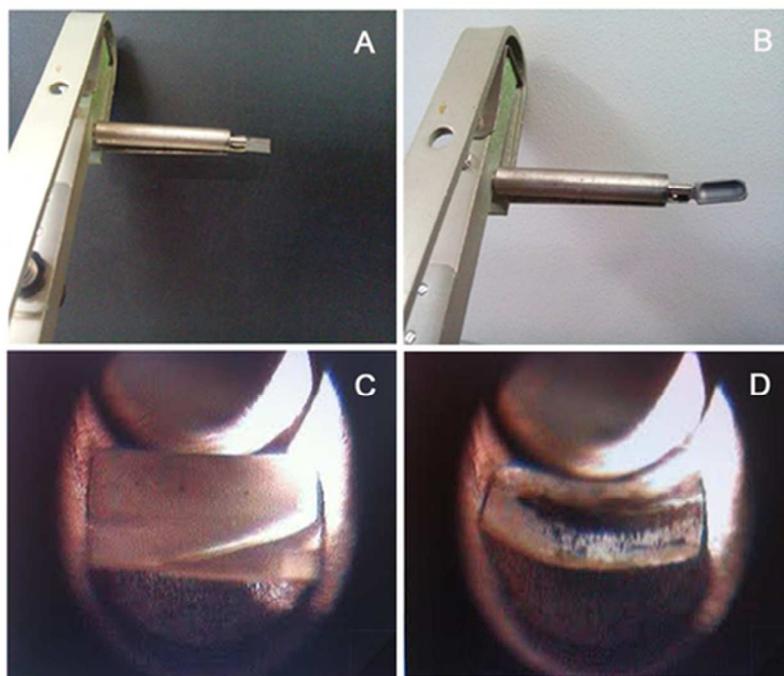377

378

379 **Figure captions**

380 Fig. 1. Introduction of (A) the TPS platform and (B) the graphite platform using the

381 manual SS accessory; (C) and (D) show the position of the TPS platform inside the

382 graphite tube; picture taken with the video camera of the contra 600; (C) empty TPS

383 platform, (D) TPS platform with solid sample.
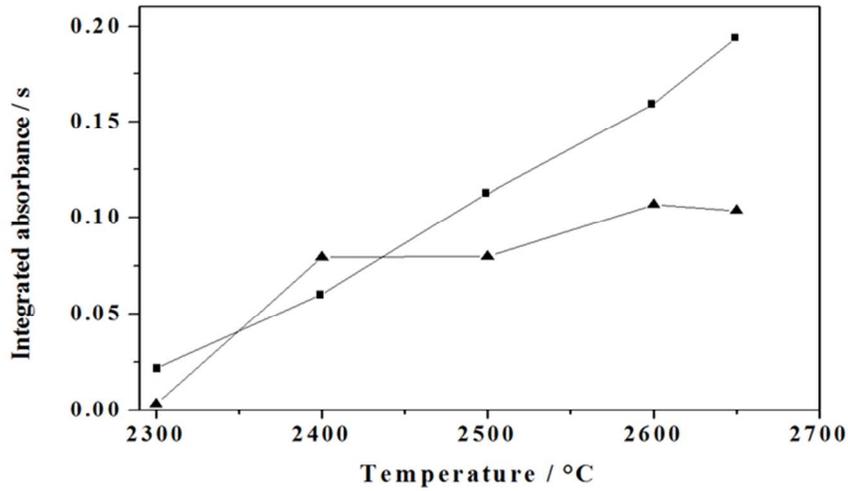
384 Fig. 2. Atomization curves for 0.4 ng Mo (■) and 1.0 ng V (▲) in aqueous standard

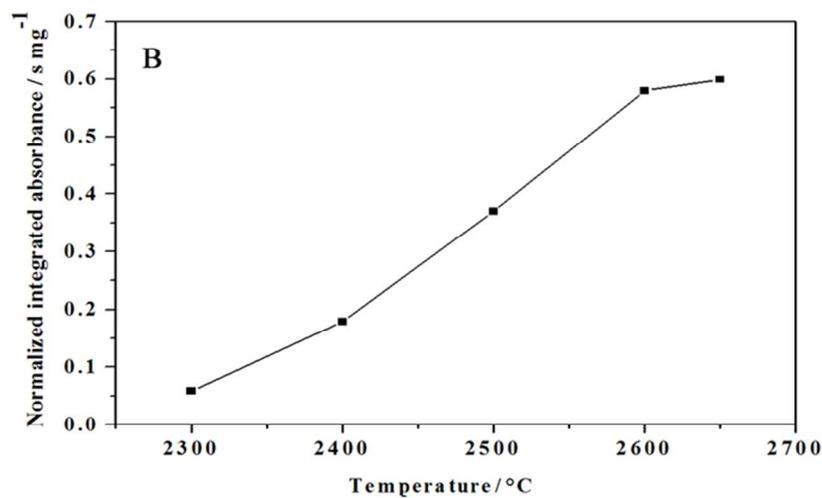385 solution. Pyrolysis temperature was fixed at 1200 °C for Mo and 1100 ºC for V.

386 Fig. 3. Atomization curves for: (A) Mo – about 0.07 mg of CRM NIST 1649a (≈ 1 ng of

387 Mo); and (B) V – about 0.7 mg of CRM IAEA 336 (≈ 1 ng of V) on the TPS platform.

388 All integrated absorbance values normalized for 1 mg of sample weight. Pyrolysis

389 temperature of 1200 °C for Mo and 1100 ºC for V.

390 Fig. 4. Comparison of absorbance signals for about 0.07 mg of CRM NIST 1649a

391 (≈ 1 ng Mo), deposited on TPS film and graphite platform, respectively. (A)

392 Superimposed absorbance signals measured at the CP at 313.259 nm using a TPS film

393 (solid line) and a graphite platform (broken line). (B) and (C): time-resolved absorbance

394 spectra using: (B) TPS film and (C) conventional graphite platform; $T_{Pyr} = 1200$ °C and

395 $T_{At} = 2650$ °C.

396 Fig. 5. Comparison of absorbance signals for about 0.7 mg of CRM IAEA-336

397 (≈ 1 ng V), deposited on TPS film and graphite platform, respectively. (A)

398 Superimposed absorbance signals measured at the CP at 318.398 nm using a TPS film

399 (solid line) and a graphite platform (dotted line), respectively. (B) and (C): time-

400 resolved absorbance spectra using: (B) TPS film and (C) conventional graphite

401 platform; $T_{Pyr} = 1100$ °C and $T_{At} = 2600$ °C.

402   Fig. 6. Comparison of absorbance signals for approximately 0.3 ng Mo; solid line:

403   ≈ 0.02 mg of CRM NIST 1649a, introduced on a TPS film; broken line: 15 μL of

404   20 μg L^{-1} Mo solution injected directly onto the tube wall. T_{Pyr} = 1200 °C and T_{At} =

405   2650 °C.

406   Fig. 7. Comparison of absorbance signals for approximately 1.3 ng V; solid line:

407   ≈ 0.9 mg of CRM IAEA-336, introduced on a TPS film; broken line: 6.5 μL of 200 μg

408   L^{-1} V solution injected directly onto the tube wall. T_{Pyr} = 1100 °C and T_{At} = 2600 °C.

409   Fig. 8. Comparison of absorbance signals for Mo in ≈ 0.22 mg of CRM NIST 1649a

410   after eight atomization cycles; solid line: TPS film platform; dotted line: graphite

411   platform; T_{Pyr} = 1200 °C and T_{At} = 2650 °C. Both measurement cycles started with new

412   graphite tubes, and in the case of the graphite platform with a new platform.

413

414

Fig. 1. Introduction of (A) the TPS platform and (B) the graphite platform using the manual SS accessory; (C) and (D) show the position of the TPS platform inside the graphite tube; picture taken with the video camera of the contra 600; (C) empty TPS platform, (D) TPS platform with solid sample.
50x36mm (300 x 300 DPI)

Fig. 2. Atomization curves for 0.4 ng Mo (ν) and 1.0 ng V (▲) in aqueous standard solution. Pyrolysis temperature was fixed at 1200 °C for Mo and 1100 ºC for V.
70x39mm (300 x 300 DPI)
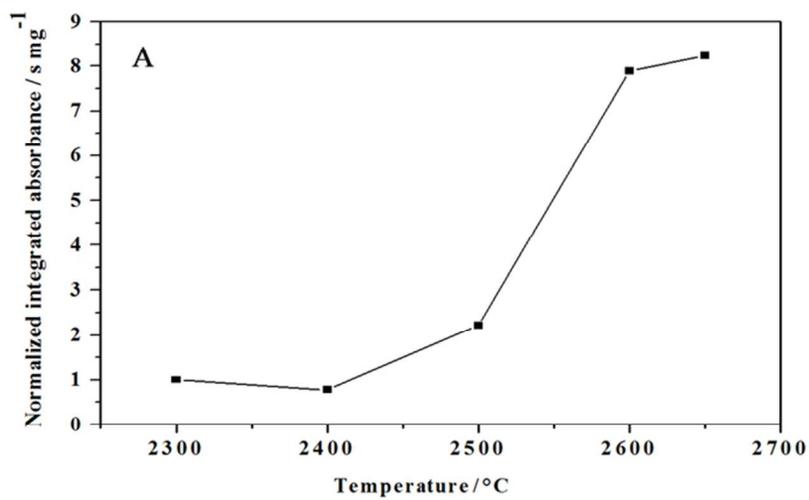
70x39mm (300 x 300 DPI)

Fig. 3. Atomization curves for: (A) Mo – about 0.07 mg of CRM NIST 1649a (≈ 1 ng of Mo); and (B) V – about 0.7 mg of CRM IAEA 336 (≈ 1 ng of V) on the TPS platform. All integrated absorbance values normalized for 1 mg of sample weight. Pyrolysis temperature of 1200 °C for Mo and 1100 ºC for V. 70x39mm (300 x 300 DPI)
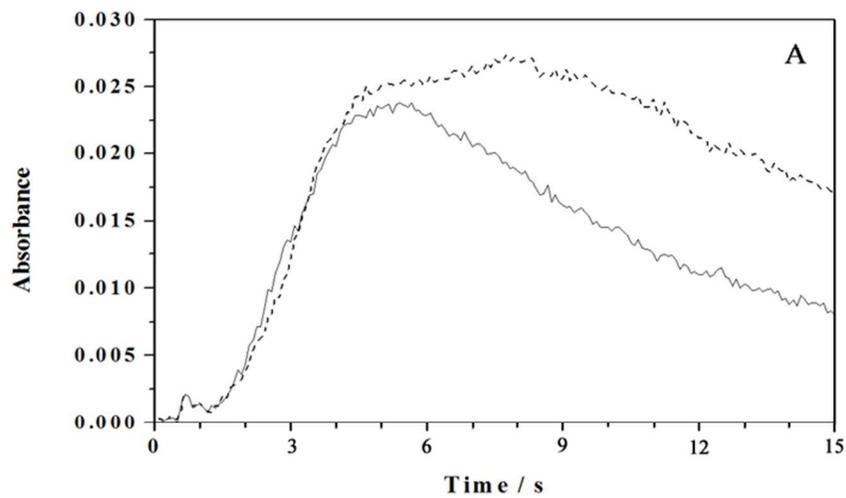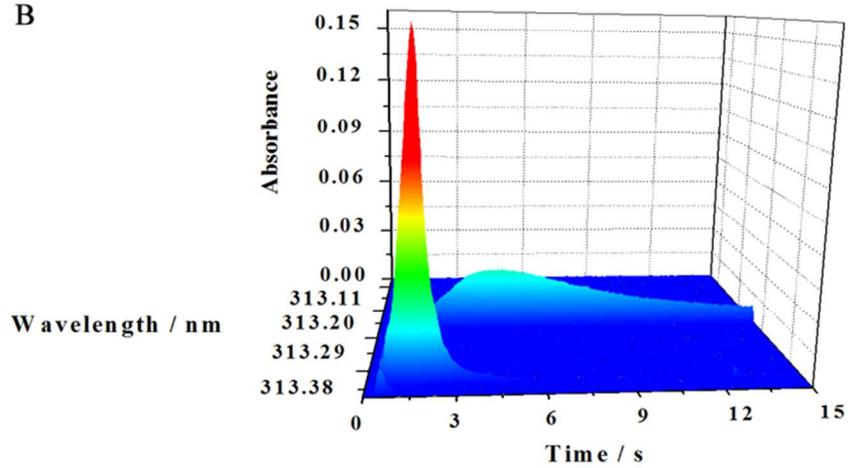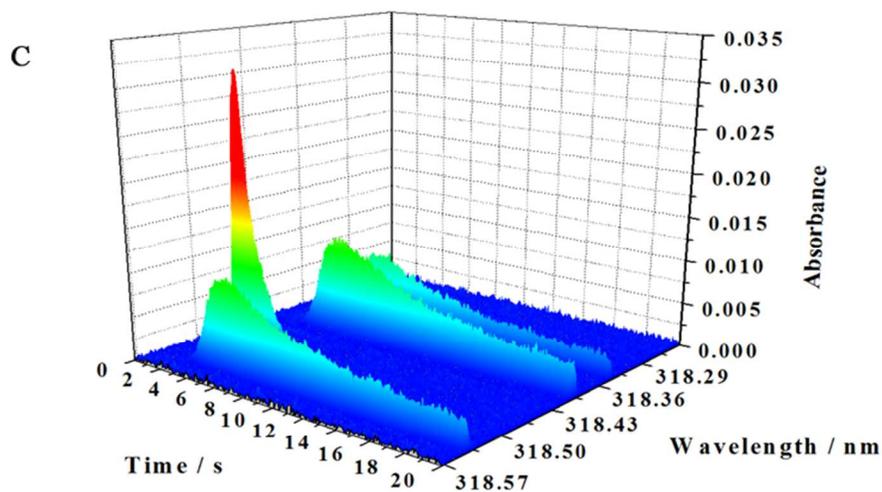
70x39mm (300 x 300 DPI)

70x39mm (300 x 300 DPI)
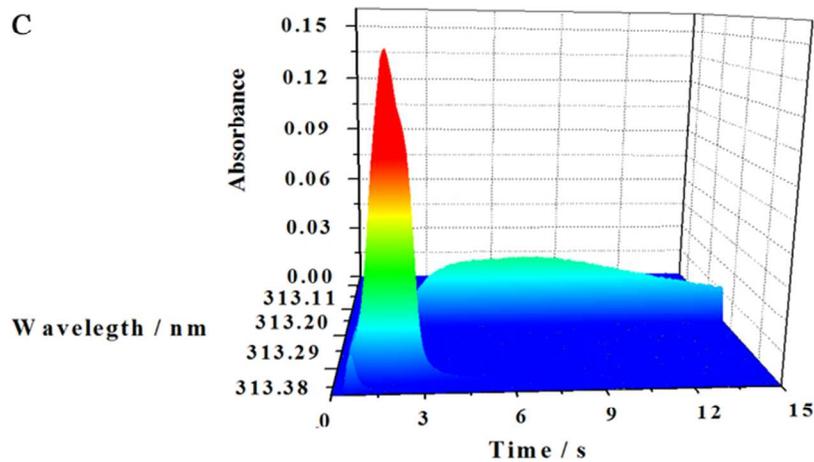
Fig. 4. Comparison of absorbance signals for about 0.07 mg of CRM NIST 1649a
(≈ 1 ng Mo), deposited on TPS film and graphite platform, respectively. (A) Superimposed absorbance signals measured at the CP at 313.259 nm using a TPS film (solid line) and a graphite platform (broken line). (B) and (C): time-resolved absorbance spectra using: (B) TPS film and (C) conventional graphite platform; TPyr = 1200 °C and TAt = 2650 °C.

70x39mm (300 x 300 DPI)

70x39mm (300 x 300 DPI)

70x39mm (300 x 300 DPI)

Fig. 5. Comparison of absorbance signals for about 0.7 mg of CRM IAEA-336 (≈ 1 ng V), deposited on TPS film and graphite platform, respectively. (A) Superimposed absorbance signals measured at the CP at 318.398 nm using a TPS film (solid line) and a graphite platform (dotted line), respectively. (B) and (C): time-resolved absorbance spectra using: (B) TPS film and (C) conventional graphite platform; TPyr = 1100 °C and TAt = 2600 °C.
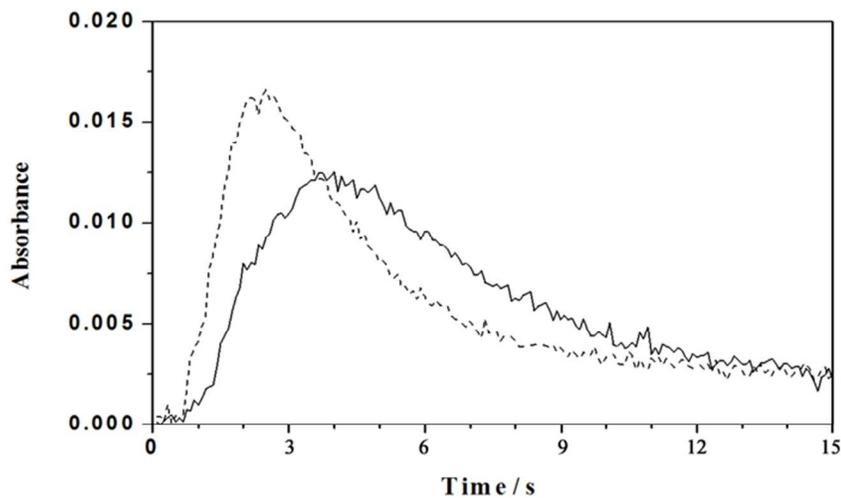70x39mm (300 x 300 DPI)

Fig. 6. Comparison of absorbance signals for approximately 0.3 ng Mo; solid line:
≈ 0.02 mg of CRM NIST 1649a, introduced on a TPS film; broken line: 15 μL of
20 μg L-1 Mo solution injected directly onto the tube wall. TPyr = 1200 °C and TAt = 2650 °C.
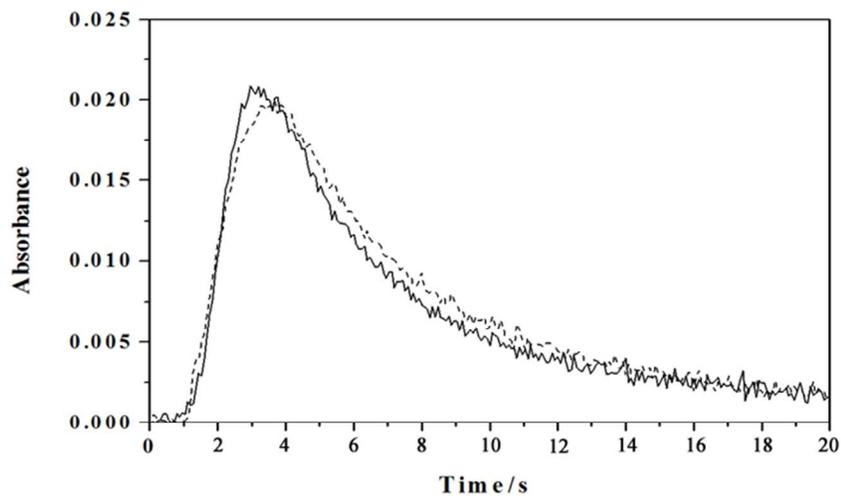
70x39mm (300 x 300 DPI)

Fig. 7. Comparison of absorbance signals for approximately 1.3 ng V; solid line:
≈ 0.9 mg of CRM IAEA-336, introduced on a TPS film; broken line: 6.5 µL of 200 µg L-1 V solution injected
directly onto the tube wall. TPyr = 1100 °C and TAt = 2600 °C.
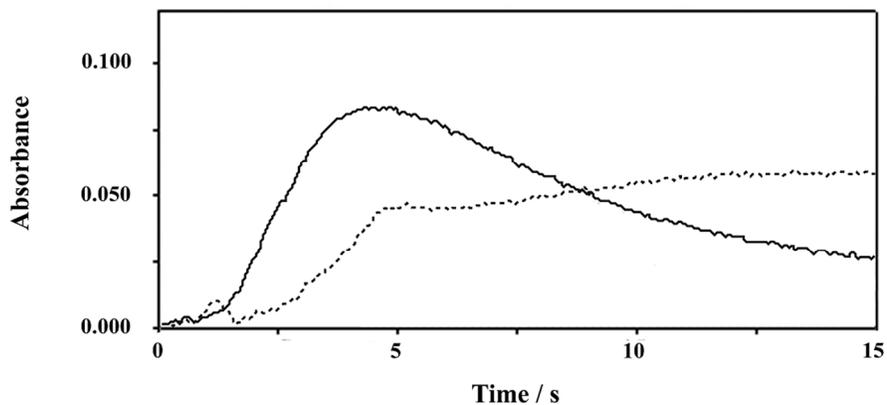
70x39mm (300 x 300 DPI)

Fig. 8. Comparison of absorbance signals for Mo in ≈ 0.22 mg of CRM NIST 1649a after eight atomization cycles; solid line: TPS film platform; dotted line: graphite platform; TPyr = 1200 °C and TAt = 2650 °C. Both measurement cycles started with new graphite tubes, and in the case of the graphite platform with a new platform.
104x46mm (300 x 300 DPI)