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Analytical note

Evaluation of solid sampling for determination of Mo, Ni, Co, and V in soil by high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

New methods are proposed for the determination of Mo, Ni, Co, and V in soils using high-resolution continuum source graphite furnace atomic absorption spectrometry with direct solid sampling. Cobalt and V were simultaneously determined, and different analytical lines of Ni and V were monitored to adjust sensitivity for each sample. Accuracy was checked by means of soil certified reference materials, and also by flame atomic absorption spectrometry as comparative technique. The results for Mo, Ni, Co, and V found by proposed methods were in agreement with certified values and with those obtained by the comparative technique at 95% confidence level. The concentrations found in different soil samples were in the ranges 0.19–1.84 mg kg^{-1} (Mo), 9.2–22.7 mg kg^{-1} (Ni), 1.1–10.7 mg kg^{-1} (Co), and 35.6–426.1 mg kg^{-1} (V). The relative standard deviations were in the ranges 3.2–10% (Mo), 2.8–9.8% (Ni), 4.0–9.2% (Co), and 1.2–8.0% (V). The limits of quantification for Mo, Ni, Co, and V were 0.027, 0.071, 0.15, and 1.43 ng, respectively.

1. Introduction

The analysis of soil fertility is essential in agricultural management practices in order to ensure high productivity and quality of agricultural crops [1]. The elements Mo, Ni, Co, and V are directly related to the biogenic cycle of nitrogen: Mo, Co, and V are involved in the biological fixation of nitrogen by soil bacteria [2–4], while Ni deficiency in the soil can lead to the accumulation of urea in plants [5]. So, the monitoring of Mo, Ni, Co, and V in agricultural soils may contribute to best management practices for nitrogen fertilizers, with benefits from both ecological and economic perspectives.

According to the National Environment Council (CONAMA) Resolution 460/2013 [6], the United States Environmental Protection Agency (US EPA) official method 3052 [7] is recommended for determination of Mo, Ni, Co, and V in soils, which requires wet decomposition of the sample based on use of hazardous reagents. In addition to wet decomposition, the method 3052 recommends the determination of Mo, Ni, Co, and V by atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES) or inductively coupled plasma mass spectrometry (ICP-MS).

Solid sampling-electrothermal atomic absorption spectrometry (SS-ETAAS) is a feasible and attractive alternative to both conventional AAS methodologies using sample decomposition and slurry ETAAS [8,9]. The solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (SS HR-CS GFAAS) [10] circumvented limitations related to the stability of slurries in conventional line source ETAAS. Indeed, the SS HR-CS GFAAS has the possibility of monitoring multiple lines, improving background correction based on least-squares algorithm and integrating automatic solid sampler and microbalance, which may reduce errors caused by manual operations [10]. The SS HR-CS GFAAS has been applied in soil analysis for determination of Cd and Fe [11,12], Cd, Cr, Fe, Al [13], Se [14], Sb [15], Ag [16]. However, the literature is lacking in reports concerning the determination of Co, V, Mo and Ni in soil by SS HR-CS GFAAS.

Hence, this work describes the development of analytical methods for the determination of Mo, Ni, Co, and V in soils by SS HR-CS GFAAS exploring the simultaneous determination of Mo and Ni, and the monitoring different lines of Ni and V in order to fit the sensitivity for each sample.

2. Experimental

2.1. Instrumentation

The Mo, Ni, Co, and V absorbance measurements were performed using an Analytik Jena ContrAA 700 graphite furnace atomic absorption spectrometer (Jena, Germany) equipped with solid sampling tubes. The lines selected for the absorbance measurements were 313.259 nm (Mo), 341.347 and 341.477 nm (Ni), 304.400 nm (Co), and 304.355

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and 304.494 nm (V). The peak volume selected absorbance (PVSA) [17] was equivalent to three pixels (central pixel ± adjacent ones). The graphite furnace heating programs for the determination of Mo, Ni, Co, and V are provided in Table 1.

An AnalytikJena contrAA 300 high-resolution continuum source atomic absorption spectrometer equipped with a xenon short-arc lamp operating in a hot-spot mode was used as comparative technique. Air-acetylene and nitrous oxide-acetylene flames were used for atomization of Co and Ni, and Mo and V, respectively. The aspiration rate was fixed at 5 mL min^{-1} and the equipment was adjusted to provide best sensitivity. All measurements were carried out under optimum conditions in three replicates using an injection module (SFS 6) enabling the computer-controlled aspiration of blanks, analytical solutions and samples.

The samples were weighed directly onto solid sampling platforms using a WZ2PW microbalance (Sartorius, Göttingen, Germany) with an accuracy of 0.001 mg. The platforms were then inserted into the graphite furnace using an SSA 600 solids autosampler (Analytik Jena). High purity argon (99.999%, White Martins, Sertãozinho, Brazil) was used as the purge and protection gas.

The samples were dried in a forced air circulation oven (Te-394/2, Tecnal, Piracicaba, Brazil). A Spex 6800 cryogenic mill (Metuchen, USA) was used to grind the soil samples.

2.2. Reagents, analytical solutions, and samples

All solutions were prepared using high purity water (18.2 MΩ cm resistivity) obtained from a Rios 5® reverse osmosis system and a Milli-Q ™ Academic® deionizer (Millipore, Bedford, USA). Nitric acid (Suprapur® grade) was from Merck (Darmstadt, Germany).

Working standard solutions containing 0.062 mg L^{-1} Mo, 2.2 mg L^{-1} Ni, 100 mg L^{-1} Ni, 0.50 mg L^{-1} Co, and 4.0 mg L^{-1} V were prepared using suitable dilutions of stock standard solutions containing 1000 mg L^{-1} Ni, Co, and V, and 100 mg L^{-1} Mo (Specsol, São Paulo, Brazil), acidified with 0.1% (v/v) HNO_3.

Chemical modifier solutions containing 2000 mg L^{-1} $Mg(NO_3)_2$ or 30% (w/v) NH_4F, together with 0.05% (w/v) Triton X-100 (Mallinckrodt, Paris, USA) were prepared by dissolving suitable quantities of Suprapur® $Mg(NO_3)_2 \cdot 6H_2O$ (Merck) or NH_4F (Merck) in water.

The accuracy of the method was evaluated by means of the following certified reference materials (CRM): 2709a (San Joaquim Soil) and 2711a (Montana Soil II), from the National Institute of Standards and Technology (Gaithersburg, USA); IAEA-SOIL-7 Trace Elements in Soil, from the International Atomic Energy Agency (Vienna, Austria); and GBW07104 Rock Constituents, from the China National Analysis Center for Iron and Steel (Beijing, China).

Six soil samples provided by a soil fertility laboratory in São Gotardo (Minas Gerais, Brazil) were dried at 65 °C for 72 h in a forced air circulation oven. A portion of the sample was then transferred to a milling vessel, immersed in liquid nitrogen, and ground using a six-step procedure: 2 min freezing; 3 min grinding; 2 min freezing; 3 min grinding; 2 min freezing; 3 min grinding. This resulted in a material with particle size ≤100 μm.

2.3. Analytical procedure

The graphite furnace heating program was optimized by evaluating the thermal behaviors of Mo, Ni, Co, and V by means of a full factorial design with two factors (pyrolysis and atomization temperatures) and two levels called minimum (−) and maximum (+). Table 2 shows the experimental matrix used for the optimization. The optimization of experiments was performed in random order using a soil sample, with masses in the ranges 0.15–0.20 mg (Mo) and 0.10–0.15 mg (Ni, Co, and V), in the absence (for Mo) and presence of $Mg(NO_3)_2$ (for Ni) and NH_4F (for Co and V) as modifiers. The absorbance was measured in triplicate ($n = 3$) and then normalized for use as the analytical response. The experimental data obtained from the factorial design were processed using Statgraphics Centurion XVI software (v. 16.1.15), generating a mathematical function whose maximization corresponded to the ideal analytical conditions used in the graphite furnace heating program for single (Ni, Mo) or simultaneous (Co, V) determination in the subsequent experiments.

Analytical curves were constructed in the mass ranges 0–0.54 ng (Mo), 0–500 ng (Ni), 0–5.0 ng (Co), and 0–40 ng (V), obtained by adding different amounts of working standard solutions (0.062 mg L^{-1} Mo, 2.2 mg L^{-1} Ni, 100 mg L^{-1} Ni, 0.50 mg L^{-1} Co, and 4.0 mg L^{-1} V). The first point of the calibration curves, corresponding to a concentration of 0 ng, was obtained employing the notion of zero mass, with a platform that was empty (except for the presence of modifiers, when required).

The influence of the soil matrix on the sensitivity of the method was evaluated by constructing calibration curves for aqueous and solid media in the ranges 0–0.54 ng (Mo), 0–500 ng (Ni), 0–5.0 ng (Co), and 0–40 ng (V). These curves were obtained using different amounts of working standard solutions (aqueous media) or different masses of the GBW07104 Rock Constituents (Mo: 0.1–1.0 mg) and 2711a Montana Soil II (Ni: 0–0.5 mg; Co, V: 0–0.75 mg) CRMs (solid media). Each point of the curves corresponded to the average of measurements in triplicate.

The minimum mass for the determination of Mo was investigated using a mass range of 0.05–1.0 mg and the GBW07104 Rock Constituents CRM. The minimum masses for determination of Ni, Co, and V were investigated using mass ranges of 0.05–0.5 mg and the 2711a Montana Soil II CRM. The minimum masses for determination of Co, Mo, Ni and V were also investigated using mass ranges of 0.05–0.55 mg and soil sample #5 containing 0.63 ± 0.02 mg kg^{-1} Mo, 16.3 ± 1.6 mg kg^{-1} Ni, 4.7 ± 0.4 mg kg^{-1} Co, 81.1 ± 6.5 mg kg^{-1} V. The absorbance readings were obtained in increments of 0.1 mg, with each value corresponding to the average of measurements in triplicate.

The limits of detection (LOD) and quantification (LOQ) were determined according to the IUPAC recommendations [18]: $3 \times SD^{blank}/b$ (LOD), and $10 \times SD^{blank}/b$ (LOQ), where SD is the standard deviation for ten blank measurements (using an empty platform) and b is the angular coefficient of the calibration curve.

For the determination of Mo, Ni, Co, and V by SS HR-CS GFAAS, soil masses between 0.15 and 0.25 mg were transferred to the platform, weighed, followed by addition of modifiers (except for Mo) and

Table 1
Optimized graphite furnace heating programs for determining Mo, Ni, Co and V in soil samples by SS HR-CS GFAAS.

Step	Mo				Ni				Co and V			
	Temp. (°C)	Ramp (°C/s)	Hold time (s)	Argon flow rate (L/min)	Temp. (°C)	Ramp (°C/s)	Hold time (s)	Argon flow rate (L/min)	Temp. (°C)	Ramp (°C/s)	Hold time (s)	Argon flow rate (L/min)
Drying 1	130	15	20	2	110	10	20	2	100	6	10	2
Drying 2	300	20	20	2	250	15	10	2	250	10	35	2
Pyrolysis	1600	50	15	2	1500	100	10	2	1500	150	10	2
Auto-zero[a]	1600	0	5	0	1500	0	5	0	1500	0	5	0
Atomization	2650	3000	12	0	2650	3000	10	0	2650	3000	10	0
Cleaning	2650	0	4	2	2650	0	5	2	2650	0	5	2

[a] Step used to record a series of baseline spectra immediately before atomization.

Table 2
Experimental matrix used to evaluate the effects of pyrolysis and atomization temperatures on the determination of Mo, Ni, Co, and V in soil samples.

Variables								
Experiments[*]	Pyrolysis temperature (°C)				Atomization temperature (°C)			
	Levels	Mo	Ni	Co and V	Levels	Mo	Ni	Co and V
1	−	1400	1300	1300	−	2550	2550	2500
2	+	1600	1500	1500	−	2550	2550	2500
3	−	1400	1300	1300	+	2650	2650	2650
4	+	1600	1500	1500	+	2650	2650	2650

[*] n = 3.

introduced automatically into the graphite furnace. For the determination of Ni, 20 μg of $Mg(NO_3)_2$ was added as a chemical modifier, while 1.5 mg of NH_4F was used as modifier for the joint determination of Co and V. All the measurements were performed in triplicate (n = 3).

3. Results

3.1. Evaluation of analytical lines

The main Mo line at 313.259 nm was chosen due to the low levels of Mo (0.1–5 mg kg^{-1}) usually found in soils [19]. Considering the wide ranges of concentrations of Ni (4–2000 mg kg^{-1}) and V (3–310 mg kg^{-1}) found in different soil types [20,21], it was decided to monitor the triplets of these elements (Ni: 341.347, 341.394, and 341.477 nm; V: 304.312, 304.355, and 304.494 nm). Since the triplets present different sensitivities (Fig. 1), the linear working ranges could be extended simply by simultaneously measuring the different lines. In the HR-CS GFAAS, all measurements were performed simultaneously, the most suitable lines were used to determine Ni and V, without any need to reprocess the sample under other instrumental conditions. Despite the low relative sensitivities of the Ni line at 341.347 nm (0.42%) and the V line at 304.494 nm (2.2%), both lines were useful for the determination of these analytes in some samples.

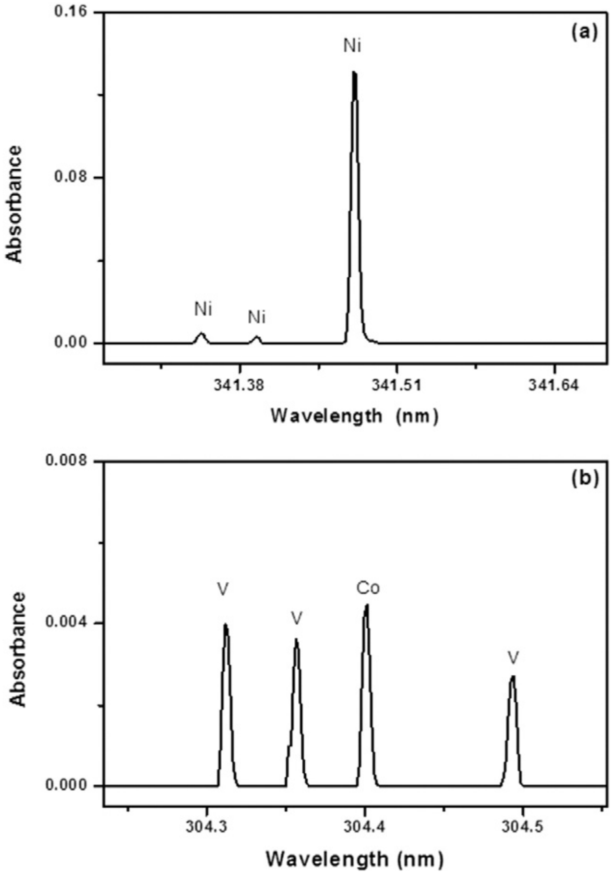

Fig. 1. Absorbance spectra for standard solution containing (a) 50 ng Ni and (b) 2 ng Co + 16 ng V. Heating program shown in Table 1.

The selected Co line at 304.400 nm also showed low relative sensitivity (6.3%), but enabled the determination of Co in soils at concentrations in the approximate range 1–40 mg kg^{-1} [3]. It can be seen in Fig. 1 that the Co line at 304.400 lies in the same spectral window as the V triplet, so the absorbance of Co and V could be measured simultaneously.

3.2. Use of chemical modifiers

Preliminary investigations were conducted to evaluate the need to use chemical modifiers in the measurements. The selection of $Mg(NO_3)_2$ and NH_4F as chemical modifiers in this work was based on previous studies [21].

In the case of Mo, the profiles of the transient signals obtained for the aqueous medium and soil were similar (Fig. 2a), indicating similarity in the release of the analyte into the vapor phase. Hence, it was not necessary to use a chemical modifier for the determination of Mo.

The profile of the transient atomic absorption signal for Ni obtained for the soil sample without addition of a chemical modifier (Fig. 2b) showed a broad double peak, indicating that matrix components caused slower release of the analyte to the vapor phase, at two different times. The addition of $Mg(NO_3)_2$ significantly improved the rate of appearance of the transient signal and its return to the baseline, resulting in a profile that was very similar to the Ni signal obtained for the aqueous sample (Fig. 2b). This was probably due to the efficiency of the $Mg(NO_3)_2$ modifier in extracting Ni from the interior to the surface of the soil matrix, facilitating the vaporization of $Ni_{(g)}$. $Mg(NO_3)_2$ was therefore used as a chemical modifier in subsequent Ni measurements.

The influence of NH_4F was investigated in measurements of 2 ng of Co and 16 ng of V, varying the mass of the modifier between 0 and 3 mg. In the absence of the modifier, the Co transient signal obtained using soil showed multiple peaks and a slow return to the baseline, indicative of a significant influence of the matrix on Co vaporization. The presence of the modifier improved atomization and the profile of the transient signal, with the best results achieved using NH_4F amounts exceeding 1.5 mg. The absorbance measured in the presence of NH_4F was around 90% higher than without the modifier. The profiles of the Co transient signals were similar for aqueous and solid media, although the sensitivities were different (Fig. 2c). In the case of V, in the absence of the modifier the release kinetics were slower for the solid medium, compared to the aqueous medium. Effective modification of the solid matrix was achieved using 1.5 mg NH_4F, with the atomic absorption signal profile for the solid medium becoming similar to that observed for the aqueous medium (Fig. 2d). The presence of NH_4F was therefore important in subsequent experiments involving the determination of Co and V in soils. Afterwards, the thermal behavior of analytes were evaluated in the absence (for Mo) and presence of $Mg(NO_3)_2$ (for Ni) and NH_4F (for Co and V) as modifiers.

3.3. Thermal behaviors of Mo, Ni, Co, and V

The thermal behaviors of Mo, Ni, Co, and V were evaluated through the pyrolysis and atomization temperatures, whose levels combination were established according to a 22 factorial design, in order to obtain the best compromise temperatures. The maximum and minimum levels of studied factors were selected based on literature data [10,22] and the monitored responses were the normalized integrated absorbance. The experimental results were processed using the Statgraphics Centurion XVI software.

For the determination of Co and V, the individual analytical responses were used to identify the optimum conditions for the joint

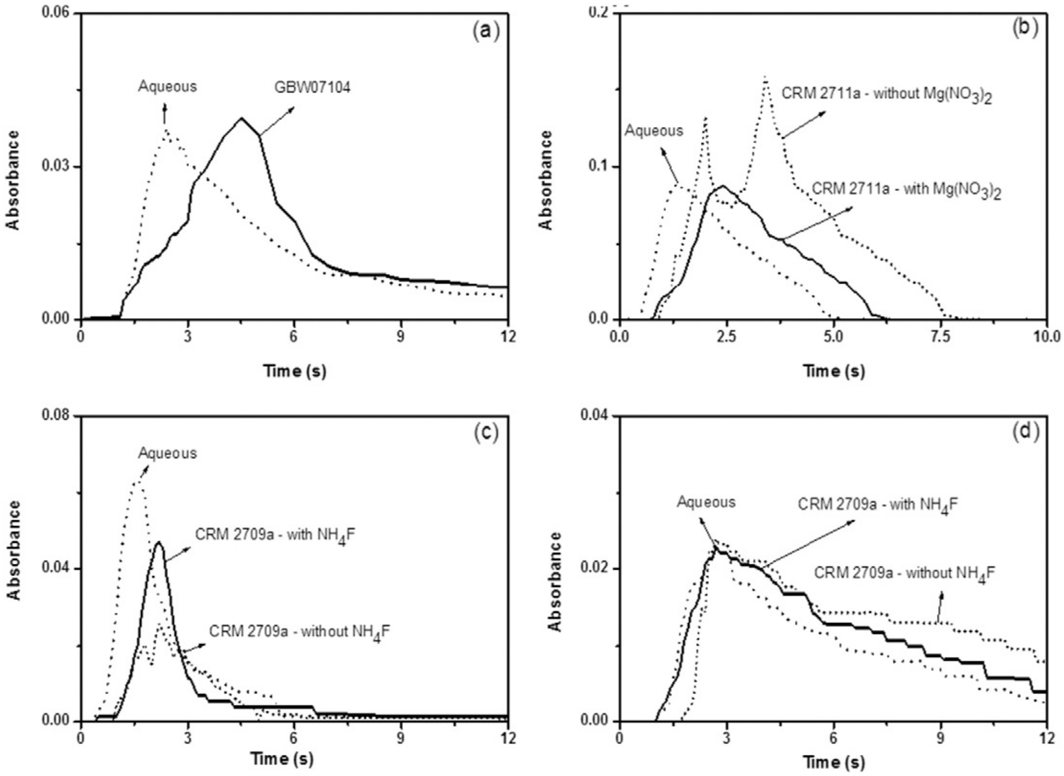

Fig. 2. Signal profiles obtained for the atomization of Mo, Ni, Co, and V in aqueous and solid media: (a) 0.33 ng Mo, (b) 2.0 ng Ni, (c) 2.0 ng Co, and (d) 16 ng V. Heating program shown in Table 1.

determination of these elements. In the case of Co, no significant effects of the factors on the analytical response were observed (at 95% confidence level), while for V only the atomization temperature showed a significant positive effect. The possible precursor to V(g) is VC(s) [22], which explains the higher temperature required for atomization. In the case of Mo, only the atomization temperature presented a significant positive effect, indicating that the analytical response was maximized at the highest level. This was probably because the precursor of Mo(g), MoC(s) [22], is refractory in nature and requires high temperatures for its dissociation during the atomization step. For Ni, significant positive effects were found for the atomization temperature and the interaction between the pyrolysis and atomization temperatures. Ni(g), whose atomic precursor is possibly NiO(s) [22], also presents refractory characteristics, hence explaining the maximization of the response using atomization at the highest level. The analytical responses obtained under the different experimental conditions were used to generate a mathematical model considering the effects and interactions of the variables, from which a contour plot was constructed to establish the compromise temperatures for the individual determinations of Mo and Ni and the joint determination of Co and V. The temperatures for pyrolysis (Tp) and atomization (Ta), respectively, were 1600 and 2600 °C (Mo), 1500 and 2650 °C (Ni), and 1500 and 2650 °C (Co and V). These values were adopted in the subsequent experiments.

3.4. Minimum mass and homogeneity

The precision and accuracy of the microanalysis of solid samples by HR-CS GFAAS are affected by the size of the sample [23]. The influence of sample mass on the accuracy of the measurements was evaluated by analyzing different amounts of the reference materials, as follows: 0.05–1 mg of GBW07104 Rock Constituents (for Mo); 0.05–0.5 mg of 2711a Montana Soil II (for Ni); and 0.05–0.75 mg of 2711a Montana Soil II (for Co and V); 0.05–0.55 mg of sample #5 (for Co, Mo, Ni and V). Results were obtained with greater precision and accuracy using the following masses of the CRMs: 0.15–0.20 mg (for Mo) and 0.10–0.15 mg (for Ni, Co, and V). And best results for the determination of Co, Mo, Ni and V in sample #5 were obtained for the mass range of 0.15–0.25 mg. Masses within these ranges were weighed out and used in the determinations. The homogeneity at micro scale may be evaluated by means of the homogeneity factor $H_e = S_H. m^{1/2}$, in which S_H is the sampling uncertainty and m the sample mass. Materials may be considered homogeneous when H_e is lower than 10 [23]. The CRM and sample tested were considered homogeneous for selected mass ranges, since calculated H_e factors were below 10.

3.5. Assessment of possible matrix effects

The influence of matrix effects on the absorbance of Mo, Ni, Co, and V was investigated by comparing the slopes of the curves obtained for concentrations in the ranges 0–0.54 ng (Mo), 0–500 ng (Ni), 0–5.0 ng (Co), and 0–40 ng (V), using either aqueous or solid standards (Mo: GBW07104 Rock Constituents; Ni, Co, and V: 2711a Montana Soil II). Good linear correlation coefficient (r) values were obtained for the response curves of Mo (aqueous: 0.9985; solid: 0.9964), Ni (aqueous: 0.9975; solid: 0.9963), V (aqueous: 0.9992; solid: 0.9953), and Co (aqueous: 0.9979; solid: 0.9987). The angular coefficients (s) of these curves and the characteristic masses (m_0) calculated for the aqueous and solid media showed no significant matrix effects for Mo (aqueous: $s = 0.449$ s ng^{-1}, $m_0 = 0.0090$ ng; solid: $s = 0.431$ s ng^{-1}, $m_0 = 0.0089$ ng), Ni (aqueous: $s = 0.095$ s ng^{-1}, $m_0 = 0.045$ ng; solid: $s = 0.096$ s ng^{-1}, $m_0 = 0.044$ ng), and V (aqueous: $s = 0.0073$ s ng^{-1}, $m_0 = 0.43$ ng; solid: $s = 0.0075$ s ng^{-1}, $m_0 = 0.41$ ng). In the case of Co, a significant matrix effect was indicated by differences in the angular coefficient and m_0 values calculated for the aqueous and solid media (aqueous: s = 0.066 s ng^{-1}, m_0 = 0.057 ng; solid: s = 0.045 s ng^{-1}, m_0 = 0.093 ng). These results indicated that the determination of the Mo, Ni, and V in soil samples could be performed using aqueous standards to construct calibration curves, while the Co calibration required the use of matrix-matched standards (the 2711a Montana Soil II CRM was used here for this purpose). As the analytical lines for Co (304.400 nm) and V (304.355 nm) were in the same spectral window, the absorbance measurements of these two elements present in the soil samples were obtained simultaneously; however, the cobalt and vanadium concentrations were calculated using the calibrations obtained for either an aqueous medium (V) or a solid medium (Co).

3.6. Figures of merit

The main figures of merit (linear range, linear correlation coefficient, angular coefficient, LOD, LOQ, characteristic mass, and precision) calculated for the calibrations using the respective analytical lines are shown in Table 3. The precision (n = 3) was calculated by using all samples. It should be mentioned that the RSD and LOD found in this work were close to published papers in the literature dealing with determination of Mo, Ni, Co, and V in soils by ETAAS employing slurry sampling [21, 24–26]. The Brazilian legislation (CONAMA Resolution #460/2013) that sets the maximum permissible concentrations of Mo, Ni, and Co in agricultural soils at 50, 70, and 35 mg kg^{-1}, respectively [6]. The legislation does not include V for agricultural land, only considering soils in industrial areas (limit value for V of 1000 mg kg^{-1}). In Table 3, if all LOQs were converted to concentrations (for typical 0.15 mg assayed samples), they are approximately 250, 140, 35 and 100 times lower than maximum permissible concentrations for Mo, Ni, Co and V, respectively. Overall, the values obtained were considered satisfactory for further development of the analytical methods for determination of Mo, Ni, Co, and V in soils employing direct solid sampling.

The accuracy of the method was subsequently evaluated by determining Mo, Ni, Co, and V in the four soil CRMs. The results obtained (Table 4) were in agreement with the certified values (Student's *t*-test, 95% confidence level).

3.7. Determination of Mo, Ni, Co, and V in soil samples

The methods were applied for the determination of Mo, Ni, Co, and V in different Brazilian soils (Table 4). The measured concentrations were in the ranges 0.19–1.84 mg kg^{-1} (Mo), 9.2–22.7 mg kg^{-1} (Ni), 1.1–10.7 mg kg^{-1} (Co), and 35.6–426.1 mg kg^{-1} (V). These concentrations were in line with the levels typically found in agricultural soils: 0.01–0.70 mg kg^{-1} Mo, 0.01–10 mg kg^{-1} Ni, 0.5–3.0 mg kg^{-1} Co, and 130–150 mg kg^{-1} V [3,19–21]. The precision (RSD) varied from 3.2 to 10% (Mo), 2.8 to 9.8% (Ni), 4.0 to 9.2% (Co), and 1.2 to 8.0% (V). Soil sample #3 showed an absorbance for V (at λ = 304.355 nm) that was above the upper limit of the linear range. As the triplet of V was measured simultaneously, the absorbance measured using the least sensitive line (at 304.494 nm) was used to simply extend the linear working range, without any need to modify the optimized instrumental conditions for an additional measurement. Hence, the total concentrations of the analytes were within the allowed limits. The results demonstrated the considerable potential of the proposed method for use as a tool to evaluate soil fertility in terms of the levels of micronutrients.

Table 3
Analytical performance parameters for determination of Mo, Ni, Co, and V by the SS HR-CS GFAAS method. Aqueous calibration was used for Mo, Ni and V, and solid standards from the *Montana Soil II* were used for Co.

Parameter	Mo	Ni		Co	V	
λ (nm)	313.259	341.477	341.347	304.400	304.355	304.494
Linear working range (ng)	0–0.54	0–8.0	0–500	0–5.0	0–33	0–40
r	0.9985	0.9975	0.9953	0.9979	0.9992	0.9981
Slope (s ng^{-1})	0.449	0.095	0.0017	0.0452	0.0073	0.0069
LOD (ng)	0.0082	0.021	1.8	0.044	0.43	0.59
LOQ (ng)	0.027	0.071	5.8	0.15	1.43	1.96
m_0 (ng)	0.009	0.045	2.45	0.093	0.43	0.64
RSD (%)	3.0–10	2.8–9.8	1.4–4.3	4.0–9.2	1.2–8.0	1.3–5.3

Table 4
Results (mean ± standard deviation, n = 3) for the determination of Mo, Ni, Co, and V (mg kg^{-1}) in CRMs and soils by the proposed SS HR-CS GFAAS methods, and soils by FAAS comparative technique. Aqueous calibration was used to determine Mo, Ni and V, and solid standards were prepared using the *Montana Soil II* to determine Co.

CRM/sample	Mo	Ni	Co[a]	V[a]
GBW07104 Rock Constituents				
Found	0.56 ± 0.02	18.2 ± 1.3	13.0 ± 0.2	90.6 ± 8.6
Certified	0.54 ± 0.14	17 ± 2	13.2 ± 1.5	94 ± 6
IAEA-SOIL-7 Trace Elements in Soil				
Found	1.64 ± 0.01	25.8 ± 1.1	10.8 ± 0.6	66.0 ± 3.3
Information	0.9–5.1	26	8.9	66
2711a Montana Soil II				
Found	–	22.6 ± 0.9	–	79.6 ± 3.8
Certified	–	21.7 ± 0.7	9.89 ± 0.18	80.7 ± 5.7
2709a San Joaquin Soil				
Found	–	85.7 ± 1.3	12.6 ± 0.8	110.1 ± 3.3
Certified	–	85 ± 2	12.8 ± 0.2	110 ± 11
Soil 1				
Found	1.84 ± 0.18	9.3 ± 0.8	<1.0	35.6 ± 0.9
FAAS	1.88 ± 0.30	9.5 ± 0.3	<1.0	36.0 ± 4.2
Soil 2				
Found	0.66 ± 0.07	17.5 ± 1.3	5.2 ± 0.3	152.2 ± 11.3
FAAS	0.63 ± 0.05	15.8 ± 1.0	5.8 ± 0.3	157.8 ± 11.1
Soil 3				
Found	0.49 ± 0.05	22.7 ± 0.6	10.7 ± 0.9	426.1 ± 22.6
FAAS	0.45 ± 0.05	23.9 ± 1.2	12.1 ± 0.2	430.5 ± 21.8
Soil 4				
Found	0.73 ± 0.05	9.2 ± 0.6	1.1 ± 0.1	35.6 ± 2.6
FAAS	0.77 ± 0.05	8.4 ± 0.4	1.2 ± 0.1	32.1 ± 3.1
Soil 5				
Found	0.63 ± 0.02	16.3 ± 1.6	4.7 ± 0.4	81.1 ± 6.5
FAAS	0.61 ± 0.03	15.9 ± 0.9	5.4 ± 0.3	87.9 ± 2.7
Soil 6				
Found	0.19 ± 0.01	14.0 ± 0.4	1.7 ± 0.1	108.0 ± 1.3
FAAS	0.23 ± 0.04	13.6 ± 0.8	1.9 ± 0.2	105.3 ± 5.6

[a] Simultaneous determination.

4. Conclusions

The proposed SS HR-CS GFAAS methodology provides a valuable tool for the determination of Mo, Ni, Co, and V in soils. The advantages of the proposed strategy based on SS HR-CS GFAAS for soil analysis, focusing on the determination of micronutrients, include: (i) simple unconventional sample preparation; (ii) representative results using very small sample amounts; (iii) rapid determination of analytes; (iv) the ability to jointly determine V and Co; (v) the ability to determine Ni in a wide range of concentrations. The proposed techniques for determination of the elements should be useful for routine laboratory analyses of soil fertility.

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