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Determination of Cadmium, Copper, Iron, Manganese, Lead and Zinc in Lichens and Botanic Samples by Electrothermal and Flame Atomic Absorption Spectrometry

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Within the framework of the International Atomic Energy Agency (IAEA) Analytical Quality Control Service (AQCS) Chemistry Unit a research program was initiated for the identification of trace elements such as Cd, Cu, Fe, Mn, Pb and Zn in IAEA lichen-338 for a proficiency test (PT). This was to evaluate the possibility of using lichens as biomonitors of trace elements in atmospheric pollution. Pyrolysis and atomization temperatures, atomization and background profiles, detection limits and characteristic masses of analytes in lichen samples with Ni, Ni + Pd and Ni + Pd + tartaric acid (TA) modifier mixture, and without any modifiers were comprehensively investigated by electrothermal atomic absorption spectrometry (ETAAS). The detection limits and characteristic masses of analytes obtained were $0.06 \mu\text{g L}^{-1}$ and 2.04 pg for Cd, $1.26 \mu\text{g L}^{-1}$ and 18.4 pg for Pb, $0.66 \mu\text{g L}^{-1}$ and 6.4 pg for Cu, $0.16 \mu\text{g L}^{-1}$ and 1.42 pg for Mn in ETAAS with (Ni + Pd + TA), and $72.1 \mu\text{g L}^{-1}$ for Fe and $20.1 \mu\text{g L}^{-1}$ for Zn in flame atomic absorption spectrometry (FAAS). Cd, Cu, Pb and Mn in tomato leaves (1573a) from the National Institute of Standards and Technology (NIST) and hay powder (V-10) from IAEA certified reference materials (CRMs) and in lichen samples by ETAAS with Ni + Pd + TA, and Fe and Zn by FAAS were determined. The results obtained in CRMs were in good agreement with the certified values and the recoveries were about 100%.

Key Words: Lichen, ETAAS, Ni + Pd +TA, Copper, Iron

Introduction

Lichens are effective biomonitors for metal deposition related to the atmospheric pollution by metals^{1,2}. Lichens are slow growing and assimilate metals at a rapid rate but release them at a low rate. The ability of absorbing and accumulating this type of pollutant from the air, associated with their longevity and resistance

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to environmental stresses, make lichens suitable for studies on air quality assessment¹⁻³. Concentrations of metals in lichen samples have been shown to correlate with atmospheric levels. Lichens have also been used to assess the deposition of heavy metals in large-scale monitoring. In lichens, metals can accumulate to high levels by trapping insoluble particles, extracellular ion exchange processes, adsorption and active uptake.

Direct determination of trace and toxic heavy metals such as Cd, Pb, Cu, Mn, Fe and Zn in botanic samples has been important and has caused great interest in recent years due to human exposure and environmental parameters such as air pollution⁴⁻⁶. The analytical techniques employed most often for the determination of analytes in samples are flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) due to their high sensitivity, selectivity and simplicity⁴⁻⁸. However, there are some difficulties in the determination of analytes by ETAAS due to high background absorption and interference effects in the sample matrix. Chemical modification, platform atomization and a powerful background correction technique have been used to minimize both background absorption signals and interference effects in real samples prior to the atomization stage⁵⁻⁹. The chemical modifiers such as Ni, Pd, Pt, Ni + Pd, Ni +Pd + TA and Ni +Pd + NH₄H₂PO₄ have been used for the stabilization of analyte elements^{10,11}. Pyrolytically coated graphite tubes with platforms and Zeeman effect background correction are also favorable and essential for the direct determination of trace elements in such samples¹⁰.

Microwave-assisted acid decomposition of samples is often performed in a microwave oven in order to reduce mass loss of analytes and to increase the sample dissolution rate¹². Addition of both nitric acid and hydrogen peroxide for dissolving samples is preferred to reduce carbonaceous residues^{10,13}.

The IAEA AQCS Chemistry Unit (Seibersdorf) intended to organize a proficiency test (PT) for the determination of a number of elements in 2 lichen materials with approximately 150 laboratories including ours. In this work, the results of our participation are presented. The standards, measurements and testing program of IAEA proposed the use of lichen as the certified reference material for the provision of accurate results and error minimization¹⁴. The purpose of this circular was to identify laboratories that would be interested in participating in this exercise. The samples sent by IAEA are IAEA lichen -338 (Lichen PT material coded 146A) and IAEA quality control lichen material (Lichen test material coded 146B), taken from mountainous regions in Western Europe, and IAEA trace element solution (standard solution of trace elements coded 146C). Tomato leaves (1573a) from NIST and hay powder (V-10) from IAEA were also analyzed by FAAS- ETAAS in order to check the accuracy and precision. Ni + Pd + TA modifier mixture¹¹ was used for the thermal stabilization and determination of Cd, Pb, Cu and Mn in samples. Pyrolysis and atomization temperatures, interference effects on atomization profiles of analytes in samples, characteristic masses (m_o) and limits of detection (LOD) were compared in the presence or absence of modifiers. Fe and Zn in samples were determined by FAAS.

Experimental

Instrumentation

All absorbance measurements of analytes were carried out with a Hitachi Model 180/80 flame and graphite furnace (Hitachi 180/78) atomic absorption spectrometer equipped with a Zeeman effect background corrector, an autosampler (P/N-170/126) and an automatic data processor. Instrumental parameters for analytes were set as recommended by the manufacturer. Single element hollow cathode lamps of analytes from Hi-

tachi were used as radiation sources. Graphite platforms (P/N-190/6008) inserted into pyrolytically coated graphite tubes (P/N-190/6007) were used to measure absorbance values using integrated mode throughout. Argon 99.99% (v/v) was used as carrier gas during all stages except for atomization. The optimized graphite furnace temperature program for the determination of Cd, Cu, Pb and Mn by ETAAS using Ni + Pd + TA modifier mixture is given in Table 1. The volume of sample or standard together with the modifier mixture injected into the platform was 20 μL . An acetylene-air flame was used in FAAS for the determinations of Fe and Zn.

Table 1. Heating program for Cd, Pb, Cu, Mn determination in sample digests with different modifiers.

Step	Temperature ($^{\circ}\text{C}$)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Dry-1	50-130	30	-	250
Dry-2	130-200	20	10	250
Pyrolysis	200-Variable ^a	30	30	250
Atomization	Variable ^b	0	7	0
Cleaning	Variable ^c	0	3	250

^a See Table 2. ^bOptimum atomization temperatures for Cd, Pb, Cu and Mn found are 1500, 2000, 2700 and 2500 $^{\circ}\text{C}$, respectively. ^c Cleaning temperatures used are 2650 $^{\circ}\text{C}$ for Cd, Pb and Mn, and 2800 $^{\circ}\text{C}$ for Cu.

A Varian Model 9176 recorder was used in a 20 mV/FS span in order to obtain atomization and background signal profiles. A Milestone Ethos Sel microwave oven (MLS Ethos-1600, Italy) equipped with 120 mL Teflon digestion vessels with holders, a removable 10-position sample carousel, a computer program and a hose to permit venting of fumes into a fume hood was used. Pressure and temperature sensors were connected to one vessel. To ensure similar amounts of microwave energy for all samples, the sample carousel was rotated 180 $^{\circ}$ forwards and backwards by an internal motor.

Reagents and standards

All reagents were of analytical reagent grade. Deionized water obtained from an ultra pure water system (Nanopure Infinity, Barnstead, P/N-1161, $\geq 18 \text{ M}\Omega \text{ cm}$) was used for the preparation of aqueous solutions throughout. Nitric acid 65% (w/w), H_2O_2 35% (w/w), HF 40% (w/w) and H_2SO_4 96-98% (w/w) extra pure grade acids (Merck, Darmstadt, Germany) were used to dissolve the solid samples. All plastic bottles, autosampler cups and glassware materials were cleaned thoroughly with detergent solution, soaked in nitric acid 20% (v/v) for 2 days, rinsed 6 times with deionized water and dried.

A nickel(II) stock solution (6.0 mg mL^{-1}) in 1% (v/v) nitric acid was prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ (Merck). A stock standard solution of Pd (2.0 mg mL^{-1}) was prepared by dissolving 506 mg of palladium nitrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, Merck) in 1 mL of concentrated nitric acid and diluting to 100 mL. A 4% (m/v) tartaric acid (TA) solution was prepared in deionized water. Stock standard solutions of Cd, Cu, Mn, Pb, Fe and Zn (1.0 g L^{-1}) from BDH Chemicals (Poole, UK) were used and working standard solutions were freshly prepared by suitable dilution in 0.2% (v/v) nitric acid before use.

Decomposition of samples

A sufficient amount of sample (0.25-2.00 g) was weighed into a petri dish and heated in an oven at 105 $^{\circ}\text{C}$ for 2 h in order to determine moisture contents. Arithmetic means of moisture contents found are 4.0%

for PT material, 4.3% for lichen test material, 4.5% for tomato leaves and 4.2% (m/m) for hay powder. Decomposition of 6 replicates of lichen samples, and 2 replicates of tomato leaves and hay powder samples using a microwave-assisted method in closed vessels (Milestone Ethos, 1600) was performed according to the procedures described earlier¹⁵⁻¹⁸. After drying at 105 °C for 2 h, a portion of sample (0.20-1.50 g) was accurately weighed into a Teflon digestion vessel, and 4.0 mL of concentrated nitric acid, 2.0 mL of H₂O₂ and 1 mL of HF were subsequently added to the vessel^{19,20}. Using the oven program, the sample was firstly heated from room temperature to 130 °C for 5 min and kept at this temperature for 10 min (up to 900 W). Secondly, temperature was increased from 130 to 200 °C over 10 min and held for 20 min (up to 1000 W). Thirdly, the oven was turned off and the contents were kept inside for 20 min. After cooling and withdrawing the contents, the opened vessel was placed on a hot plate, 1 mL of concentrated H₂SO₄ was added and the sample was gently boiled to near dryness in order to evaporate the excess acids such as HF. If a residue remained, the decomposition procedure mentioned above was repeated until complete decomposition was achieved. The resulting solution was subsequently transferred into a 25 mL volumetric flask by adjusting the final acidity with 0.5% (v/v) HNO₃. After adding 2 mL of HNO₃, 1.5 mL of H₂O₂ and 1 mL of HF, the Teflon vessel was heated using the microwave heating program and the procedure mentioned above and blank solutions were prepared to correct for any analyte contaminants in the reagents used during sample dissolution.

Optimum conditions

One milliliter of lichen-338 sample solution having a sufficient concentration of analyte was added to 1 mL of modifier solution (3.0 g L⁻¹ Ni, 0.4 g L⁻¹ Pd, 3.0 g L⁻¹ Ni + 0.4 g L⁻¹ Pd or 3.0 g L⁻¹ Ni + 0.4 g L⁻¹ Pd + 20 g L⁻¹ TA). Twenty microliters of sample solution together with or without of the modifier were injected into the platform.

Results and discussion

Thermal stabilization studies of analytes

Thermal stabilities of analytes in sample solutions with or without the modifiers were studied. Pyrolysis and atomization temperature curves for analytes in lichen-338 sample solutions were studied using optimum mass of modifiers or no modifier (Figure 1). The maximum pyrolysis temperatures obtained are also given in Table 2. Using these pyrolysis temperatures and the optimized heating temperature program given in Table 1, the effects of mass and mass ratio of modifiers on absorbance values of analytes in samples were investigated and they were found to be 30 µg Ni, 4 µg Pd, 200 µg TA, 30 µg Ni + 4 µg Pd + 200 µg TA for individual and mixed modifiers¹¹. As can be seen in Table 2, maximum pyrolysis temperatures of analytes in samples obtained using (Ni + Pd + TA) modifier mixture are enough to remove a significant part of matrix components without the risk of analyte loss. The use of a platform together with modifier mixture delays the vaporization of sample until the tube reaches a high stabilization temperature, thus minimizing vapor phase interferences²¹. Maximum pyrolysis temperatures of analytes in the samples obtained were compared with those in previous studies^{10,11} and similar results were observed. The differences in absorbance values may be dependent on the reactivity of analytes in samples with or without a modifier mixture. Pyrolysis and atomization temperature curves for the analytes obtained are shown in Figure 1 as examples. In the

absence of a modifier, Cd, Pb, Cu and Mn are lost at temperatures higher than 400 °C for Cd, 850 °C for Pb, 950 °C for Cu and 1000 °C for Mn (Table 2 and Figure 1). Addition of tartaric acid together with Ni + Pd modifier mixture has proved to be very efficient in reducing the modifiers and analytes to highly dispersed and reactive metallic forms and to eliminate interferences in samples^{10,11,22}. Atomization curves of analytes in sample solutions were obtained, while the pyrolysis temperatures were constant in the presence or absence of modifiers. The optimum atomization temperatures obtained are given in Table 1.

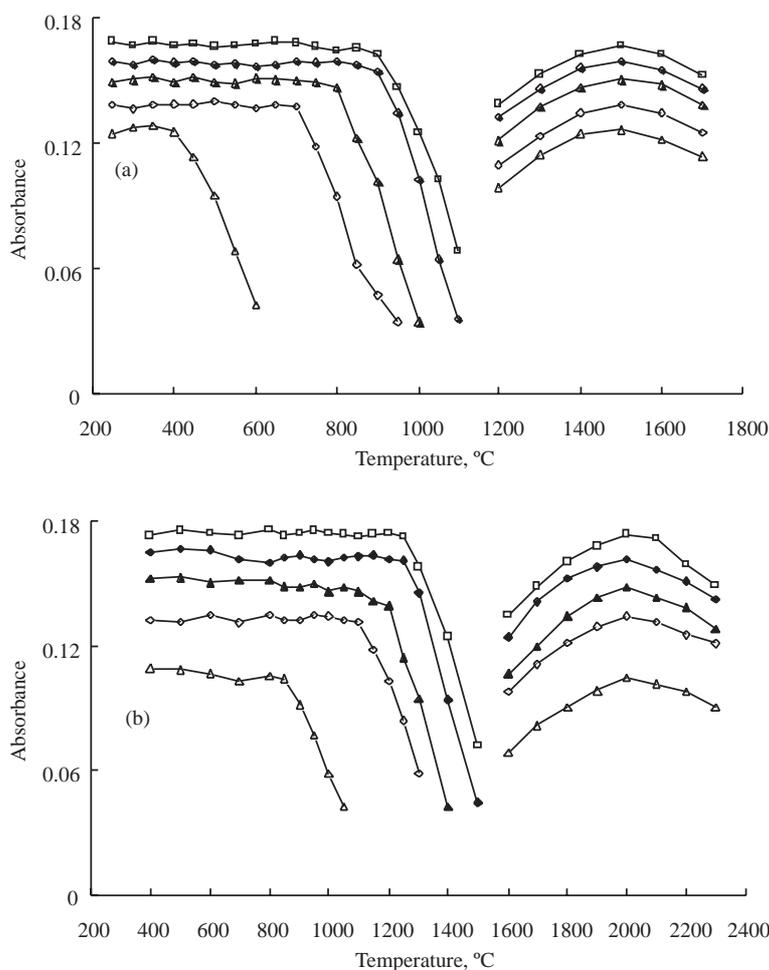


Figure 1. Pyrolysis and atomization curves for (a) Cd and (b) Pb in IAEA Lichen-338 sample solution and aqueous solutions in the absence or presence of modifiers: no modifier (Δ); $4 \mu\text{g Pd}$ (\diamond); $30 \mu\text{g Ni} + 4 \mu\text{g Pd}$ (\blacktriangle); $30 \mu\text{g Ni} + 4 \mu\text{g Pd} + 200 \mu\text{g TA}$ in sample solution (\blacklozenge) and aqueous solution for Cd ($4 \mu\text{g L}^{-1}$) and for Pb ($40 \mu\text{g L}^{-1}$) (\square). Pyrolysis and atomization temperatures of analytes obtained with or without of the modifier were given in Tables 1 and 2.

Atomization profiles of analytes

The atomic and background absorption profiles of analytes in sample solutions with or without Ni, Ni + Pd and Ni + Pd + TA modifier mixture were comparatively studied to demonstrate how the modifiers affect the atomization/background profiles of analytes^{10,23–25}. The analyte and background atomization profiles of Cd and Pb in lichen-338 sample solution are shown in Figure 2 as examples. Atomization signal shapes for

Cd and Pb in the sample solutions obtained with or without chemical modifiers are similar. In the presence of (Ni + Pd + TA) modifier mixture, the maximum peak times of Cd and Pb in sample solutions shifted to a later time and no reduction in atomic absorption signals was observed. Small absorbance values were obtained when no modifier was used. In the presence of (Ni + Pd + TA), the highest absorbance values and the lowest background signals were obtained and matrix effects in the samples were minimized. The signal/noise ratios of the analytes obtained were higher than those obtained in the absence of a modifier¹⁰.

Table 2. Maximum pyrolysis temperatures, detection limits and characteristic masses of analytes with different modifiers.

Modifier	Pyrolysis Temperature (°C)				LOD ($\mu\text{g L}^{-1}$)				m_o (pg)			
	Cd	Pb	Cu	Mn	Cd	Pb	Cu	Mn	Cd	Pb	Cu	Mn
No modifier	400	850	950	1000	1.79	7.84	5.61	0.87	2.81	33.4	26.2	4.74
Ni	750	1100	1150	1200	0.97	4.18	3.48	0.59	2.52	28.7	18.3	2.43
Ni+Pd	800	1200	1250	1300	0.48	2.01	1.79	0.34	2.32	23.9	11.7	1.71
Ni+Pd+TA	900	1250	1300	1400	0.06	1.26	0.66	0.16	2.04	18.4	6.4	1.42

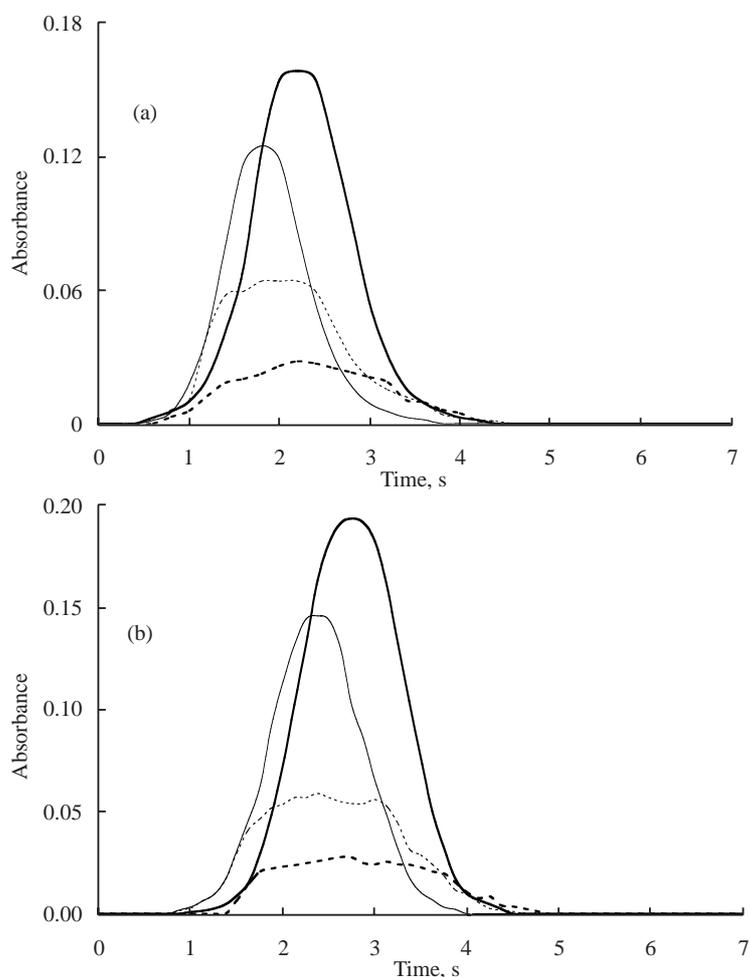


Figure 2. Atomization profiles of (a) Cd and (b) Pb in IAEA Lichen-338 sample solution; where atomization (—) and background (---) without of a modifier; atomization (—) and background (.....) profiles with 30 μg Ni + 4 μg Pd + 200 μg TA.

Analytical characteristics

The ETAAS determinations of Cd, Pb, Cu and Mn and the FAAS determinations of Fe and Zn in sample solutions were performed using calibration graphs. The calibration graphs of analytes against aqueous standard solutions were linear up to $5 \mu\text{g L}^{-1}$ for Cd, $80 \mu\text{g L}^{-1}$ for Cu and Pb and $8.0 \mu\text{g L}^{-1}$ for Mn in ETAAS with (Ni + Pd + TA) modifier mixture, and $4 \mu\text{g mL}^{-1}$ for Fe and $0.8 \mu\text{g mL}^{-1}$ for Zn in FAAS. The instrumental parameters recommended by the manufacturer were used. A standard addition technique by adding (Ni + Pd + TA) to aqueous standard solutions was also used for analytes in sample, especially for Cd and Pb, in order to check the accuracy of the proposed method. The correlation coefficients (r) for the analytes were > 0.99 .

The sensitivity in ETAAS or FAAS is expressed by means of limit of detection (LOD) and characteristic mass (m_o). The LOD is defined as the concentration of an analyte related to 3 times the standard deviation of absorbance units. The m_o is expressed as the mass of analyte corresponding to 0.0044 abs unit^{10,24,25}. The LOD (3σ -criterion) and m_o values for the analytes determined in ETAAS in the presence or absence of modifiers, and Fe and Zn in FAAS from 10 consecutive measurements of blank solutions²⁴ were calculated and the results obtained for Cd, Pb, Cu and Mn are given in Table 2. Detection limits for Fe and Zn are $72.1 \mu\text{g L}^{-1}$ and $20.1 \mu\text{g L}^{-1}$, respectively. As can be seen, better m_o values and lower detection limits were obtained in the presence of Ni + Pd + TA modifier mixture and they are similar to the results obtained in previous studies^{10,11}.

As a result of the explanations mentioned, (Ni + Pd + TA)¹¹ was used as chemical modifier mixture for the determinations of Cd, Cu, Pb and Mn lichen and botanic samples by ETAAS.

Analysis of samples

Cd, Pb, Cu and Mn in tomato leaves (1573a), hay powder (V-10) CRMs, IAEA lichen-338 (146 A), IAEA quality control lichen material (146 B) and IAEA trace element solution (146 C) were determined by ETAAS using (Ni + Pd + TA) with a heating program (Table 1) and pyrolysis temperatures obtained with Ni + Pd + TA (Table 2). Fe and Zn in samples were determined by FAAS. Using wet weights of the samples, the results obtained are given in Tables 3-5. For each CRM sample, 2 acid digested solutions were prepared and all measurements were carried out in at least 7 replicate measurements of a solution with a 95% confidence level ($t_{Student} = 2.45$) in order to determine the quality of the results. The results in Table 3 are expressed as mean \pm standard deviations (SDs) of 2 results obtained and they are in good agreement with the certified values. For each IAEA sample, 6 solutions were prepared and all absorbance measurements were carried out in at least 7 replicate measurements of a solution with a 95% confidence level. The results given in Tables 4 and 5 were also mean and SDs of 6 results obtained. The results found in samples were assessed and compared by IAEA with their own results for the proficiency test. The results obtained were accepted, except for Cu in Table 4, according to the outcome of the results. Good accuracy and precision were obtained with relative SDs lower than 10%.

Table 3. Determination of analytes in tomato leaves and hay powder.

Element Determined	Concentrations ($\mu\text{g g}^{-1}$)					
	Tomato leaves (1573a)			Hay powder (V-10)		
	Certified Value	Found ^a	Recovery (%)	Certified Value	Found ^a	Recovery (%)
Cd	1.52 ± 0.04	1.52 ± 0.05	100	-	-	
Cu	4.70 ± 0.14	4.72 ± 0.11	100	9.4 (8.8-9.7)	9.50 ± 0.28	101
Fe	368 ± 7	371 ± 6	101	185 (177-190)	182 ± 6	98
Mn	246 ± 8	247 ± 6	100	47 (32-52)	48.4 ± 1.6	103
Pb	-	-		1.6 (0.8-1.9)	1.58 ± 0.04	99
Zn	30.9 ± 0.7	31.0 ± 0.8	100	24 (21-27)	25.6 ± 0.9	107

^aMean of 7 measurements of a sample solution with a 95% confidence level, $\bar{X} \pm (ts)/\sqrt{n}$.

Table 4. Determination of analytes in IAEA Lichen-338.

Element determined	Concentrations ($\mu\text{g g}^{-1}$)		Accuracy criteria ^a		Precision ^b	Outcome
	IAEA Value	Found ^c	Bias (%)	z-Score	RSD (%)	
Cd	0.57	0.56 ± 0.02	-1.8	-0.6	5.09	Accepted
Cu	8	6.84 ± 0.04	-14.6	-4.1	5.39	Fail
Fe	900	855 ± 46	-5.0	-1.0	5.90	Accepted
Mn	52.8	54.1 ± 3.0	2.5	0.7	5.46	Accepted
Pb	57.1	55.5 ± 4.2	-2.8	1.9	5.37	Accepted
Zn	106	99.5 ± 3.8	-6.1	-1.6	5.64	Accepted

^aAccuracy criteria were calculated by IAEA; Relative bias = $(V_{Analyst}-V_{IAEA})/V_{IAEA} \times 100$; z-Score = $(V_{Analyst}-V_{IAEA})/\sigma$. ^b Precision was calculated by IAEA. ^cMean of 7 measurements of a sample solution with a 95% confidence level, $\bar{X} \pm (ts)/\sqrt{n}$.

Table 5. Determination of analytes in IAEA quality control lichen material and IAEA trace element solution.

Sample	Element determined	Concentrations ($\mu\text{g g}^{-1}$)		Accuracy criteria ^a		Outcome
		IAEA Value	Found ^b	Bias (%)	z-Score	
Quality control lichen material	Cd	0.56	0.53 ± 0.02	-6.0	-2.38	Accepted
	Cu	7.03	7.48 ± 0.03	6.4	1.74	Accepted
	Fe	804	751 ± 14	-6.6	-1.32	Accepted
	Mn	29.9	28.5 ± 0.8	-4.8	-0.97	Accepted
	Pb	40.9	40.1 ± 1.6	-2.0	-0.43	Accepted
	Zn	101	99 ± 2	-2.0	-0.51	Accepted
Trace element Solution	Cd	8.4	7.95 ± 0.34	-5.1	-1.03	Accepted
	Cu	14.4	13.5 ± 0.42	-3.7	-0.74	Accepted
	Fe	23.3	24.3 ± 0.7	4.2	0.84	Accepted
	Mn	16.2	14.6 ± 0.5	-9.6	-1.92	Accepted
	Pb	19.9	20.3 ± 0.8	1.6	0.33	Accepted
	Zn	7.1	7.16 ± 0.2	0.4	0.07	Accepted

^aAccuracy criteria were calculated by IAEA; Relative bias = $(V_{Analyst}-V_{IAEA})/V_{IAEA} \times 100$; z-Score = $(V_{Analyst}-V_{IAEA})/\sigma$. ^bMean of 7 measurements of a sample solution with a 95% confidence level, $\bar{X} \pm (ts)/\sqrt{n}$.

Conclusions

Methods were developed for the direct determination of Cd, Pb, Cu and Mn in lichen and botanic samples by ETAAS using Ni + Pd + TA modifier mixture, and Fe and Zn by FAAS. The results found in the proficiency test materials are in good agreement with the results of IAEA. It can be concluded that (Ni + Pd + TA) modifier mixture thermally stabilized Cd, Pb, Cu and Mn in samples with complex matrices. Therefore, interference effects on the determination of analytes become negligible, and the accuracy and precision are satisfactory. The (Ni + Pd + TA) modifier mixture can be considered useful for the direct determination of Cd, Pb, Cu and Mn by ETAAS in lichen and botanic samples and no further chemical treatments are necessary. The determination of Fe and Zn is also possible by FAAS without any chemical pre-treatment.

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