The use of slurry sampling for the determination of manganese and copper in various samples by electrothermal atomic absorption spectrometry

Nilgun Tokman*

Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469 Maslak-Istanbul, Turkey

Abstract

Manganese and copper in multivitamin–mineral supplements and standard reference materials were determined by slurry sampling electrothermal atomic absorption spectrometry. Slurries were prepared in an aqueous solution containing Triton X-100. The effects of different parameters such as ratio of solid to liquid phase volume, total slurry volume and addition of Triton X-100 as a dispersant on the analytical results were investigated. The graphite furnace programs were optimized for slurry sampling depending on the analytes and their concentrations in the samples. The linear calibration method with aqueous standard solutions was used for the quantification. At optimum experimental conditions, R.S.D. values were below 5%. The analytes were determined in the limits of 95% confidence level with respect to certified values in coal and soil standard reference materials and to those found by wet-digestion in multivitamin–mineral supplements. Detection limits (3δ) for Mn and Cu were $0.10\,\mu g\,L^{-1}$ and $1.82\,\mu g\,L^{-1}$ for $10\,\mu L$ coal standard reference material slurry, respectively.
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1. Introduction

Manganese is a mineral element that is both nutritionally essential and potentially toxic. A number of manganese-activated enzymes play important roles in the metabolism of carbohydrates, amino acids and cholesterol [1]. The potential sources of manganese are mining of ore, foundries, battery manufacture, welding, steel industries, pesticides and fossil fuels. The average dietary intake of manganese is approximately 11 mg/day for adults [2]. When the uptake is too high, health problems occur. High levels of manganese, which can also be inhaled by miners, may cause "manganese madness". The symptoms of manganese toxicity generally appear slowly over a period of months to years. Manganese poisoning has also been found among workers in the battery manufacturing industry. Significant rises in manganese concentrations have been found in patients with severe hepatitis and post-hepatic cirrhosis, dialysis patients and patients suffering from heart attacks. Excessive manganese can also damage the respiratory system and the male reproductive system. In its worst form, manganese toxicity can result in a permanent neurological disorder with symptoms similar to those of Parkinson's disease, including tremors, difficulty walking, and facial muscle spasms [3].

Copper is an essential trace element for humans and animals, too. It is a critical functional component for a number of essential enzymes, known as cuproenzymes. According to national surveys, the average dietary intake of copper in the US is approximately 1.0–1.1 mg/day for adult women and 1.2–1.6 mg/day for adult men [4]. Acute copper poisoning has occurred through the contamination of beverages by storage in copper containing containers as well as from contaminated water supplies [5]. Symptoms of acute copper toxicity include abdominal pain, nausea, vomiting, and diarrhea. More serious signs of acute copper toxicity include severe liver damage, kidney failure, coma, and death. Of more concern from a nutritional standpoint is the possibility of liver damage resulting from long-term exposure to lower doses of copper.

Atomic absorption spectrometry (AAS) is one of the most common methods for the determination of trace elements in all matrices. In this technique, samples are ordinarily introduced in solution form. However, even if a convenient solvent is available, dissolution/digestion of samples involves such risks and disad-

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* Tel.: +90 212 285 31 60; fax: +90 212 285 63 86.
  E-mail address: nilguntokman@yahoo.com.

vantages as contamination from reagents and vessels; analyte loss due to formation of volatile compounds during dissolution; incomplete solution; loss of time and the environmental pollution due to acid vapours during dissolution/digestion method [6,7]. In order to avoid the above-mentioned disadvantages, dissolution process is eliminated by applying solid sampling technique. Nevertheless, in solid sampling technique, sensitivity of analyte changes not only with analyte concentration, but also with the amount of sample, particle size and chemical form of analyte and composition of the matrix. In addition, high background values, calibration difficulties, weighing errors are the other drawbacks of this technique. The last but not least, solid sampling requires some special sampling devices, tubes and platforms and sensitive balances [8–16].

Another alternative for introducing solid samples into the furnace without dissolution is the slurry technique in which finely pulverized solids are introduced into the furnace as their slurries using conventional liquid sample delivery technique. This technique combines the advantages of solution and solid sampling analysis as well as eliminates their disadvantages. It is rather suitable for less-soluble solid samples such as coal, sediment, suspended solids in water, etc. [17–33]. Sample preparation is very practical. The reagents used in sample digestion procedures including corrosive mineral acids and powerful oxidizing agents are hazardous whereas only pure water or aqueous solutions are needed for slurry preparation. There is no (or low) risk of analyte loss or contamination during sample preparation. Another advantage of slurry sampling method compared to solid sampling is to change the slurry concentration by diluting. However, slurries can be diluted only to a limited extent in order to provide homogeneity in slurry and aliquots pipetted into the furnace resulting in errors.

On the other hand, the slurry sampling method is not free problems. The precision and accuracy of the analyses by slurry sampling technique depend basically on the homogeneous distribution of solid particles in the slurry, as well as its stabilization with time during the whole analysis which require the optimization of many variables, such as sample mixing, particle size, diluents, addition of stabilizing agent, liquid volume, etc. Homogenous slurry can be obtained by manually, mechanical or ultrasonic agitation, or by passing a gas stream through the sample. In addition, slurry should be stabilized using a highly viscous liquid medium, such as glycerol, viscalex, Triton X-100, etc. [7,22].

In this study, experimental parameters for the slurry sampling determination of manganese and copper in various samples by electrothermal atomic absorption spectrometry (ETAAS) were optimized. It was aimed to put forward a simple and practical procedure, which can be applied to various samples without using special tools.

2. Experimental

2.1. Apparatus and reagents

A Perkin-Elmer 3030 Zeeman Atomic Absorption Spectrophotometer equipped with an HGA-600 Graphite Furnace

was used for the determination of analyte elements. Pyrolytic graphite coated tubes with pyrolytic L'vov plaforms were used throughout this work. The wavelength was set to 324.8 nm resonance lines for Cu in coal (NIST SRM 1632b) and soil (NIST SRM 2709) samples whereas less sensitive 222.6 nm were used for the determination of Cu in multivitamin–mineral supplements and soil (NIST SRM 2711) samples. The wavelength was set to less sensitive line of 403.1 nm for the determination of Mn in all samples studied. Nitrogen was used as the purge gas. For the determination of Mn in multivitamin–mineral supplements, NIST SRM 2709 soil and NIST SRM 2711 soil; Cu in NIST 1632b coal and NIST SRM 2709 soil, gas-flow was applied during atomization step in order to decrease the sensitivity whereas for the rest of determinations, gas-flow was interrupted during the atomization step.

The graphite furnace operating parameters optimized for slurry sampling conditions are presented in Table 1. Samples were introduced into graphite furnace as 10 μL with an Eppendorf micropipette manually. Signal evaluation was performed exclusively by means of integrated absorbance values (peak area) for all determinations.

All chemicals were of analytical grade (Merck, Germany). Stock solutions $(1000 \, mg \, L^{-1})$ of Mn and Cu were prepared from Titrisol (Merck) and further diluted with distilled-deionized water daily.

The multivitamin–mineral supplements were obtained from the manufacturer (Deva Co., Istanbul, Turkey). Standard reference materials (NIST SRM 1632b Trace Elements in Bituminous Coal, NIST SRM 2709 San Joaquin Soil and NIST SRM 2711 Montana II Soil) were bought from National Institute of Standards and Technology (USA).

Results were given as the average of at least three independent replicate analyses.

2.2. Wet-pseudo-digestion procedure

Finely ground multivitamin–mineral supplements were dried in an oven at 105 °C until constant weight was reached. 1.5 g of dried sample was accurately weighed and digested using 15 mL of HNO_3–HCl $(2 + 1)$ mixtures on hot plates at 100 °C. After fil-

Table 1
Graphite furnace program for the determination of Mn and Cu by slurry technique

Step no.	Furnace temperature (°C)	Time (s)		Internal gas flow (mL min^{-1})
		Ramp	Hold	
1	110	10	15	300
2	150	5	15	300
3	Pyrolysis[a]	10	20	300
4	Atomization[b]	0	6	0[c]
5	2600	1	5	300
6	20	2	6	300

[a] 1000 °C and 800 °C for Mn and Cu, respectively.
[b] 2200 °C and 2400 °C for Mn and Cu, respectively.
[c] 100 mL min^{-1} for the determination of Mn in multivitamin–mineral supplements and Cu in NIST 1632b coal, 200 mL min^{-1} for the determination of Mn and Cu in NIST SRM 2709 soil, Mn in NIST 2711 soil.

tration and dilution appropriately, the analytes were determined by ETAAS.

2.3. Slurry preparation

In order to prepare slurry, standard reference materials or multivitamin–mineral supplements were dried at 105 °C, powdered and sieved as 50 mesh. Around 10 mg of sample was weighed precisely in polyethylene autosampler cups. Samples were slurried in 250 μL in distilled-deionized water (chosen optimum) containing 20 μL of Triton X-100. The slurries were stirred with tip of pipette in order to further provide better homogenization before pipetting. Finally, 10 μL of slurry was pipetted into the atomizer manually and the analyte elements in samples were determined by ETAAS applying the instrumental parameters given in Table 1. Standard calibration method without needing any modifier was used for quantification.

3. Results and discussion

3.1. Optimization of furnace program

In order to obtain the furnace program for slurry sampling given in Table 1, several parameters, such as pyrolysis and atomization temperatures, gas-flow rates in the atomization step were investigated. When the concentrations of analytes were too high to work in linear working range with their most sensitive resonance lines, the sensitivity was reduced by applying gas-flow in the atomization step and/or using less-sensitive wavelengths. 100 mL min^{-1} of gas-flow was applied for the determination of Cu in NIST 1632b coal sample and Mn in multivitamin–mineral supplements whereas 200 mL min^{-1} of gas-flow was applied in the atomization step for the determination of Mn and Cu in NIST SRM 2709 soil and Mn in NIST SRM 2711 soil in order to reduce the sensitivity. When the determination of an analyte in a sample was made with gas-flow, the standards were atomized applying gas-flow as well. Since, the analytes in the sample and standards were atomized at the same conditions, there is no problem with respect to accuracy of results. After a set of experiments for the optimization of graphite furnace program for gas flow during atomization step, it was found that there was no need to change the temperature of the atomization step for gas-flow mode with respect to that for gas-stop mode.

3.2. Optimization of slurry preparation

Homogenization of slurry and its durability directly influence the quality of analytical results with respect to precision and accuracy. It is required the conditions to be flexible for different variety of samples and the method to be simple and practical without needing special tools. Therefore, every attempt was made to obtain completely homogeneous and durable slurries, which stay stable for long time at least during its pipettings.

In order to obtain stable homogeneous slurries of samples, the ranges of the amount of solid phase and total slurry volume were optimized. Moreover, grinding of solid sample thoroughly, addition of surfactants and effective mixing were other important criterions for homogeneous and durable slurry to obtain repetitive results.

3.2.1. Surfactant and grinding

It is known that the grinding of solid sample and the use of surfactants to increase the surface tension are helpful to provide homogeneous and stable slurries, as well as to pipette the samples successfully. In order to provide a better durability of slurry, Triton X-100 was essentially added into the slurry as a surfactant. Actually the addition of any surfactant is mandatory for all slurry sampling analyses. In the absence of any surfactant, the slurry solution was not stable for a long time because precision of results was deteriorated rapidly after a few pipettings. As expected, the addition of Triton X-100 remarkably improved the stabilization of homogeneous suspension with time during its whole analysis, providing reproducible results with less than 5% R.S.D. at optimum experimental conditions. Therefore, throughout this work, Triton X-100 was added into the slurries. For an effective stabilization, the ratio of Triton X-100 to total slurry by volume should be at least 1/12.5.

On the other hand, if the dimensions of particles are greater than diameter of pipette tip, slurry cannot be drawn or injected and it is easily clogged. Therefore, the particle size is limited with diameter of pipette tips. For slurry sampling, the lower the particles size the higher the precision. The general problem with smaller pore size is that if the sample is not homogeneous with respect to ease of grinding, then the powdered sample sieved may not represent the average of whole sample. Therefore, in order to represent the samples better, and to make the method usable for other heterogeneous samples, the possibility of applying higher pores, i.e. lower mesh sizes, were tested.

Coal, multivitamin–mineral supplements and soil were ground with agat mortar and sieved as 50 mesh (<0.28 mm) which is the biggest pored sieve in the laboratory. If the precision of repetitive pipettings were good enough for 50 mesh, it would be better for higher mesh sizes (smaller pores). It was seen by naked eye that the particles were homogeneously distributed throughout the slurry and stayed stable during the whole analysis. The small (at least satisfactory) standard deviations found in this study mean that the analyte distribution in CRM and mineral supplement powder, as well as the distribution of powdered material in slurry are homogeneous and stabilization of slurry with time are good enough to obtain low standard deviations. Since, the mesh size used seem to have no problem with respect to analytical parameters, throughout this study, the particles sieved from 50 mesh were preferred for slurry preparation without further investigating the effect of particle size on analytical parameters.

As mentioned previously, the slurry was stirred manually with pipette tip in the sample vial a few seconds prior to pipetting one more time and then it was delivered to graphite furnace as 10 μL manually. In this case, without using special tools for mixing, correct and reproducible results were obtained. However, in case of using more effective mixing tools, experimental parameters would have been more flexible.

After preparation of slurries, during the whole analysis no precipitate to be measured with naked eye was observed because

in the beginning of each manual injection, slurry solution was gently mixed or stirred with pipette. The low standard deviations for repetitive pipettings support this observation, which is the aim of the preparation of suitable slurry. However, the sedimentation curves for coal, multivitamin–mineral tablets and soils slurries were constructed. In order to obtain these curves, slurries were mixed one time before the first sampling and then let the analysis be done during 30 min without further agitation and even do not move. The samples were injected into the tube with micropipette manually. Figs. 1 and 2 show that integrated
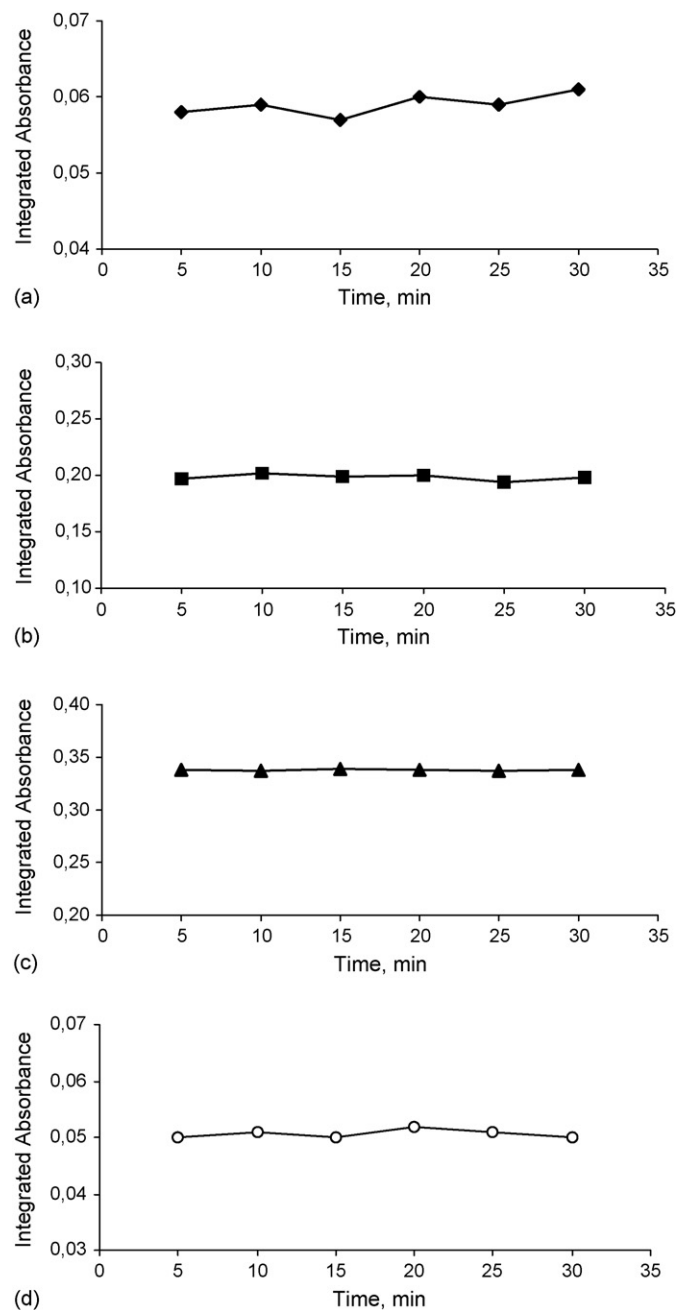

Fig. 1. Sedimentation curves for the determination of Cu in various samples: (a) NIST SRM 1632b coal (2.45 ng of Cu), (b) multivitamin–mineral supplements (184.4 ng of Cu), (c) NIST SRM 2709 San Joaquin Soil (220.1 ng of Cu) and (d) NIST SRM 2711 Montana II Soil (254.2 ng of Cu).
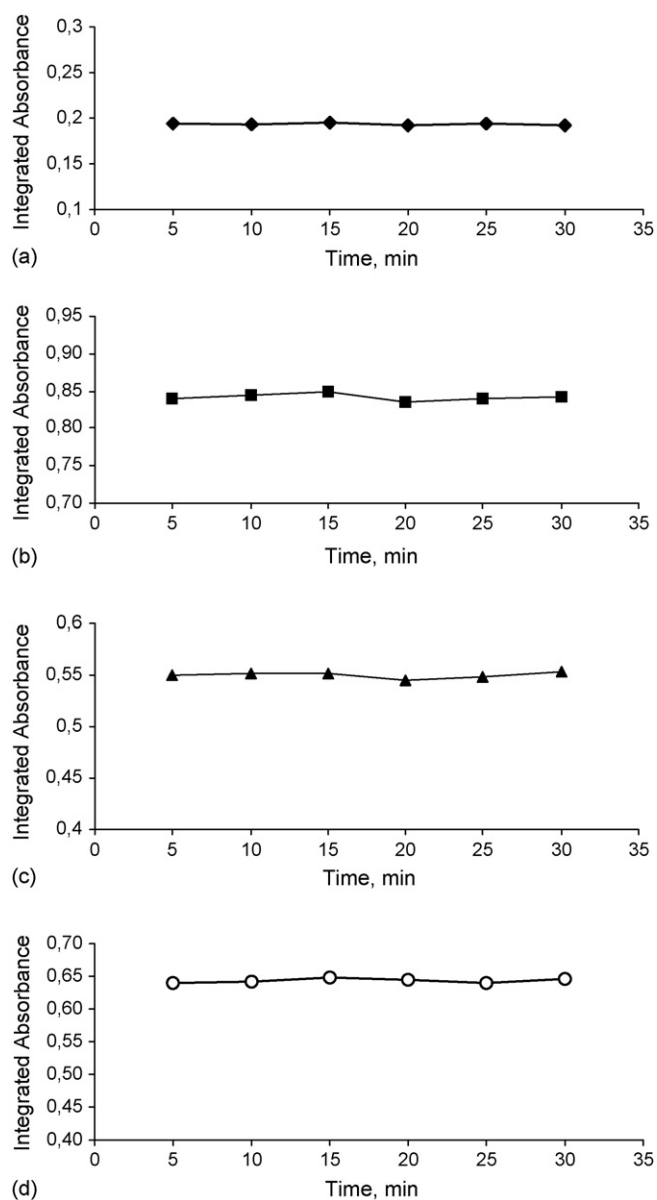

Fig. 2. Sedimentation curves for the determination of Mn in various samples: (a) NIST SRM 1632b coal (4.8 ng of Mn), (b) multivitamin–mineral supplements (76.4 ng of Mn), (c) NIST SRM 2709 San Joaquin Soil (14.3 ng of Mn) and (d) NIST SRM 2711 Montana II Soil (46.4 ng of Mn).

absorbance values obtained at the beginning of the experimental work are the same as those obtained in at least 30 min during the analysis. Namely, integrated absorbance values did not decrease with increasing sampling time. This shows that during the whole analysis slurries are homogeneous.

3.2.2. The amount of solid phase and slurry

The most critical parameter to obtain durable homogeneous slurry is the ratio of solid phase mass to slurry volume. However, in this study, it was found that individual total slurry volume was as important as the ratio of solid mass to slurry volume for the quality of analytical results, as well. This does not mean that the ratio by itself is never meaningful, but it should be considered together with individual slurry volume. It is worth to mention
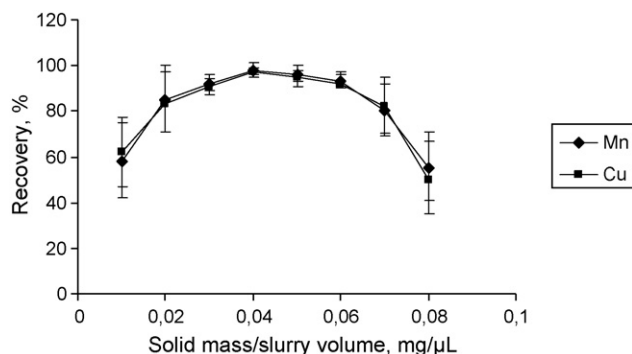
Fig. 3. The effects of the ratio of coal (NIST SRM 1632b Trace Elements in Bituminous Coal) mass to slurry volume on the recoveries of copper and manganese.

Fig. 4. The effects of slurry volume on recoveries of copper and manganese in coal (solid phase: 10 mg).

that although the solid mass is a parameter of solid mass/slurry volume ratio, homogeneity could not be obtained for all solid masses and slurry volumes even if the same ratio is kept. Therefore, although the ratio of solid mass/slurry volume was kept constant in an optimum range, if the total slurry volume was beyond the limiting values, the precision got worse and worse. For this purpose, in a series of experimental work, the effects of both absolute slurry volume and the ratio of solid mass/slurry volume on recovery (or accuracy) and precision were investigated and optimum values or ranges were determined by considering the two factors together. Obviously, the reproducibility of the number of solid particles in each aliquot taken into pipette tip is related to both the ratio of solid mass/slurry volume as well as the total slurry volume. If the volume of slurry is increased above a limit, the number of particles at every point of slurry is not the same, which deteriorates the precision. This may be originated from insufficient and unstable homogenization of slurry at experimental conditions, e.g. insufficient mixing for the homogenization of slurry completely.

The effects of the ratio of coal mass to slurry volume on the recoveries of copper and manganese are shown in Fig. 3. The total slurry volume was kept constant as 250 μL for all solid masses while solid phase masses were changed from 2.5 mg to 20 mg, which correspond to ratios of 0.01–0.08 mg μL^{-1}, respectively. The quantitative recoveries (>90%) with less than 5% R.S.D.s were obtained between 7.5 mg and 15 mg of coal in 250 μL of slurry corresponding to ratios of 0.03–0.06, respectively. However, the maximum recoveries with minimum R.S.D. were obtained for 10 mg solid phase in 250 μL corresponding to solid mass to slurry volume ratio of 0.04 with recoveries of around 97–98%. The poor precisions at lower and higher ratios beyond the optimum range in Fig. 3 as well as in Figs. 4 and 5 can be attributed to non-homogeneous distribution of solid phase and/or deterioration of homogeneity in a short time. Similar results were obtained for multivitamin–mineral supplements, too (data not shown).

The effects of slurry volume on recovery of copper and manganese in coal and multivitamin–mineral supplements are shown in Figs. 4 and 5. In these series of studies, the amounts of solid phase was kept constant as 10 mg but slurry volume was changed from 125 μL to 1000 μL. As shown from the figures, the
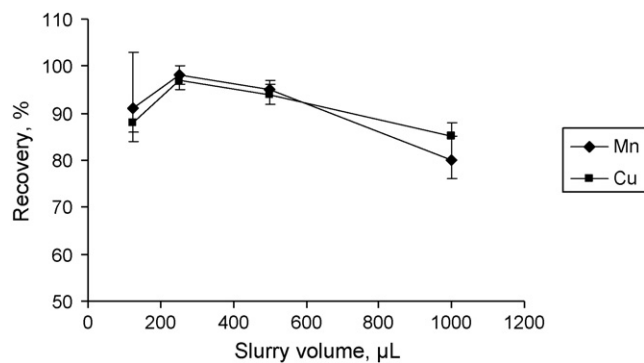
quantitative recoveries (≥95%) with less than 5% R.S.D.s were obtained at 250 μL and 500 μL, which correspond to solid mass to slurry volume ratios of 0.04–0.02 mg μL^{-1}, respectively. The most reproducible results (97–98%) with maximum recoveries (<5% R.S.D.) were obtained when 10 mg solid phase was dispended in 250 μL of slurry. When the slurry volume was increased to 1000 μL, i.e. the ratio was 0.01, the recoveries of Mn and Cu in coal and multivitamin–mineral supplements were 80–85%. On the other hand, for the same ratio (i.e. 0.01) when 2.5 mg of solid sample was dispersed in 250 μL, the recoveries and precision were worse (Fig. 3). This means that not only the ratio of solid phase to total slurry volume, but their individual absolute amounts play important roles on the quality of analytical performance, too. Consequently, 10 mg of powdered solid samples (coal, multivitamin–mineral supplements and soil) were dispersed in 250 μL of slurry for validation experiments. In this case, if the concentration of analyte at the most sensitive resonance wavelength was not suitable for the solid masses and slurry volumes determined as optimum; then instead of excessive dilution above a limit value, less sensitive wavelengths were used and/or slower heating rates and/or gas-flow during atomization step were applied to reduce the sensitivity and thereby to prepare the slurry at optimum conditions (solid mass, total volume).

In order to compensate the possible complications of imperfect experimental conditions during the preparation of slurry
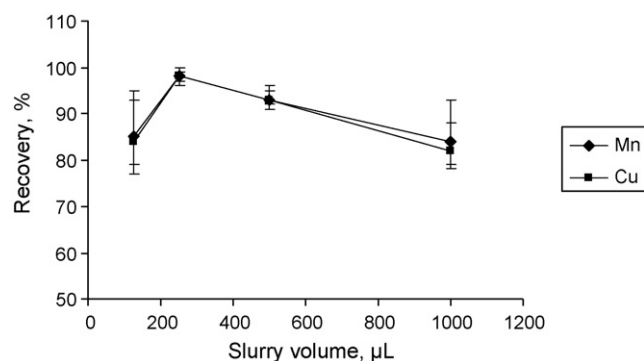

Fig. 5. The effects of slurry volume on recoveries of copper and manganese in multivitamin–mineral supplements (solid phase: 10 mg).

and to better understand if there is an interference in measurement step, all of the slurry (250 μL) was introduced into the furnace after 25 times of 10 μL pipettings, successively. By this way, all the samples were introduced into the furnace. It was hoped that even if some of the aliquots taken into the pipette tip contained less or more amount of solid phase due to non-homogeneous particle distribution, insufficient pipetting, etc., it would be retrieved in other pipettings. If recoveries had been still not quantitative, i.e. there had been still errors compared to certified (coal and soil samples) or expected (according to fortified values in multivitamin–mineral supplements) amounts, some interferences should have been occurred. The average of all pipettings was not significantly different from expected and certified values of multivitamin–mineral supplements and certified samples (coal and soil), respectively. Of course, this is a time consuming way and not the solution to the problem. It proves only that the success of the method is related to absolute and relative amounts of components of slurry rather than any interference, or errors in slurry preparations or inadequacy of other experimental parameters.

Atomic absorption signals for the both analytes in matrix-free standard solutions and in coal slurries are shown in Fig. 6. The appearance times, as well as the shapes of transients are quite similar and background values are low. Moreover, the sensitivities for analytes in matrix-free standard solutions and slurried coal samples are perfectly in agreement (almost the same). This means that without using modifier as well as standard addition method, the analytes can be correctly determined against matrix-free standards. Therefore, throughout this study, standard calibration technique was applied for quantification.

3.3. Validation of the method

The slurry method was applied to the determination of analytes (Mn and Cu) in standard reference materials (NIST SRM 1632b Trace Elements in Bituminous Coal, NIST SRM 2709 San Joaquin Soil and NIST SRM 2711 Montana II Soil) and multivitamin–mineral supplements. All data were summarized in Table 2. When 10 mg of solid sample, powdered and ground below 50 mesh, was slurried directly in vials as 250 μL of aqueous solutions containing 20 μL of Triton X-100, the results were the most consistent with those found by wet-pseudo-digestion procedure for multivitamin–mineral supplements and certified values in coal and soil. In these conditions, the results are in 95% confidence limits of certified (coal and soil) and expected (according to fortified values in multivitamin–mineral supplements during its production) values. It is important that by using the slurry conditions optimized with coal and mineral tablets, the certified values in soil samples were perfectly determined without needing further adjustment which was the main aim of this study and it was supported with this work. Detection limits, calculated as 3δ of 10 replicate analysis, for Mn and Cu were $0.10\,\mu g\,L^{-1}$, $1.82\,\mu g\,L^{-1}$ for 10 μL coal standard reference material slurry at the conditions given in Section 2, respectively.

Manganese in the same multivitamin–mineral supplements sample had been determined in the same laboratory using direct

Table 2
Analytical results for the determination of Mn and Cu in standard reference materials and multivitamin–mineral supplements by slurry sampling technique (sample volume 250 μL, solid sample 10 mg, and *N*, 3 independent analysis)

| Element	Multivitamin–mineral supplements (mg kg⁻¹)		NIST SRM 1632b (Trace Elements in Bituminous Coal) (mg kg⁻¹)		NIST SRM 2709 (San Joaquin Soil) (mg kg⁻¹)		NIST SRM 2711 (Montana II Soil) (mg kg⁻¹)	
	Found by wet-pseudo-digestion technique[a]	Found by slurry sampling technique[a]	Certified value[a]	Found by slurry sampling technique[a]	Certified value[a]	Found by slurry sampling technique[a]	Certified value[a]	Found by slurry sampling technique[a]
Mn	193 ± 5	190 ± 2	12.4 ± 1.0	11.8 ± 0.4	34.6 ± 0.7	34.8 ± 0.5	114 ± 2	115 ± 1
Cu	464 ± 6	460 ± 2	6.28 ± 0.3	6.12 ± 0.1	538 ± 17	546 ± 9	638 ± 28	630 ± 20

[a] Mean ± CL.
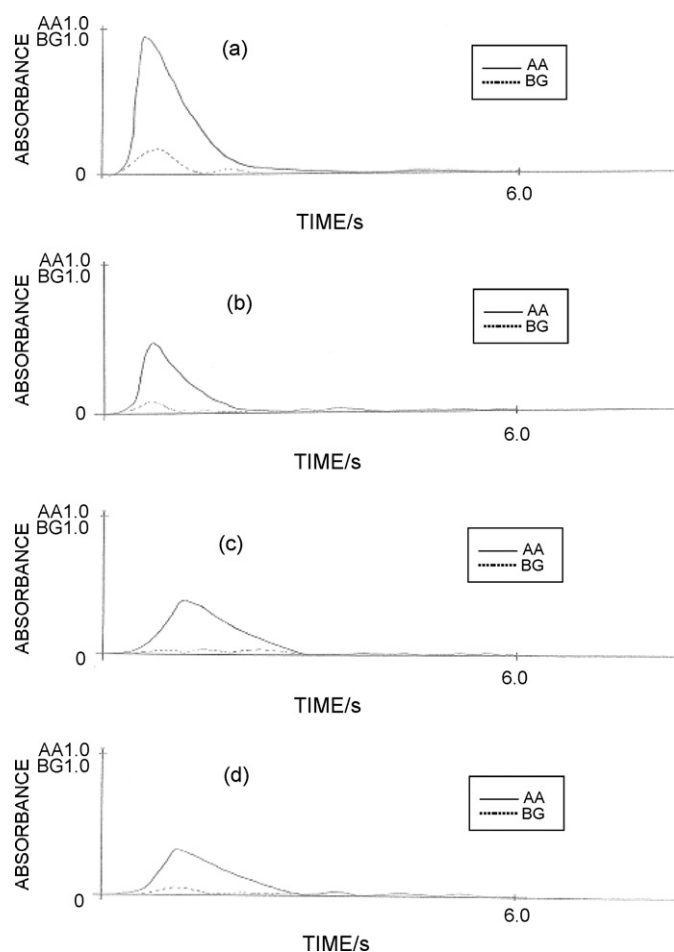
Fig. 6. Atomic absorption signals for copper in matrix-free standard solutions and in slurried coal samples: (a) manganese as the nitrate in matrix-free standard solution (integrated atomic absorbance is 0.296 for 7.50 ng of Mn; integrated absorbance per ng of Mn: 0.0395), (b) manganese in slurried coal sample (integrated atomic absorbance is 0.185 for 4.72 ng of Mn; integrated absorbance per ng of Mn: 0.0392), (c) copper as the nitrate in matrix-free standard solution (integrated atomic absorbance is 0.064 for 2.50 ng of Cu; integrated absorbance per ng of Cu: 0.0256) and (d) copper in slurried coal sample (integrated atomic absorbance is 0.061 for 2.45 ng of Cu; integrated absorbance per ng of Cu: 0.0249).

solid-sampling ETAAS method with different atomic absorption spectrophotometer, which is suitable for full automatic solid sampling [8]. If the slurry method and direct solid sampling technique are compared in all respects, the following conclusions can be drawn: (i) there are no significant differences between averages obtained by both techniques and results are in consistent with those found by dissolving the samples; (ii) slurry sampling does not need expensive extra tools which is the case for solid sampling; (iii) precision of slurry is better than that of solid sampling; (iv) slurry could be diluted (at least in a limited range as given in this study) like solutions but solids could not be diluted homogenously; (v) on the other hand, the optimization of experimental conditions for the preparation of homogenous slurry needs some effort. However, many other parameters had to be optimized in case of solid sampling technique.

4. Conclusions

Slurry technique has been applied for many samples successfully because of its many advantages over solution and solid sampling techniques. However, slurry is less often used because it needs special tools (such as high speed mixers), extra effort to optimize the experimental parameters to provide easily pipetted, completely homogenized (in micro-scale) and durable slurries. Therefore, in this study, it was aimed to manage slurry analysis with minimum effort without using special tools such as ultra fast mixers. After optimization of experimental conditions, slurry technique was successfully applied for the analysis of soil, coal and multivitamin–mineral supplements, selected as test materials, which require quite difficult and time consuming dissolution processes. It was proved that the slurry technique with the optimum conditions found in this study could be applied to many other kinds of samples without needing too much modification.

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