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Direct determination of manganese in vitamin–mineral tablets using solid sampling electrothermal atomic absorption spectrometry

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Abstract

Manganese in vitamin–minerals tablets was determined by solid sampling electrothermal atomic absorption spectrometry (SS-ETAAS) using three different calibration methods, namely calibration against aqueous standards, standard addition with aqueous standards on solid samples and calibration against solid certified standards. Samples were only finely ground and introduced directly into the furnace by means of solid autosampler system without any dissolving process. Effects of different calibration techniques, temperatures and heating rates of atomization and pyrolysis steps on the accuracy and precision of the analyte elements were investigated. After optimization of the experimental parameters, there is good agreement (at 95% confidence level) between the results obtained by solid sampling and those obtained by acid digestion of samples.

Keywords: Solid sampling; Electrothermal atomic absorption spectrometry; Vitamin tablet; Manganese; Calibration

1. Introduction

Solid sampling has always been considered as one of the most attractive features of electrothermal atomic absorption spectrometry (ETAAS). However solid sampling ETAAS (SS-ETAAS) is a very demanding type of application in several respects: manipulation and insertion of microgram to milligram masses of solid samples into the electrothermal atomizer is required; the instrumental conditions must be carefully chosen and optimized to minimize non-spectral interferences; a suitable calibration technique must be selected [1]. Direct analysis of solids can provide analysts with special information that is not obtainable by conventional techniques requiring sample dissolution, e.g. forensic applications, including analysis of gunshot residues and environmental monitoring, are well suited for solid sampling. In addition, direct solid analysis is important when only small amounts of sample are available or when there is interest in the distribution of analyte [2]. Direct determination of low concentration of elements in solids by means of ETAAS is highly attractive because of different factors. High sensitivity can be obtained, sample preparation is simple and does not involve the high risk of contaminations, or element loss as in the case of chemical pretreatments of the samples. The requirement of submilligram sample size provides the possibility of micro-heterogeneity measurements. As a consequence, it is hardly surprising that the beginning of the direct analysis of solid samples by means of AAS is almost as old as the technique itself. Today the solid sampling atomic absorption spectrometry is a routinely used analytical method of determining trace elements in biological and environmental solid samples [3].

All the interferences in solution technique can appear for solid sampling analysis too. In fact, atomization signals are assumed to be much more strongly influenced by concomitants than with solutions [4]. In many solid sampling applications, the sensitivity depends on the sample mass in the furnace. It was found that too large or too small mass of sample may lead to erroneous results [5]. This effect was not only due to deviations from linearity of Beer Law but related to the kind of matrix, size of particles, homogeneity of sample or standards and the analyte element [6]. Different explanations were made for the overestimated results obtained from small sample masses which are condensation of volatile elements on particle surfaces [7], inaccurate background correction [8] and water content in the sample [9].

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Table 1
Instrumental conditions for the direct determination of manganese in vitamin–mineral tablets

Wavelength (nm)	403.1	
Slit width (nm)	0.8	
Lamp current (mA)	5	
Temperature programme	Hold time (s)	Ramp rate ($^{\circ}C\,s^{-1}$)
Drying (120 °C)	20	25
Pyrolysis (900 °C)	20	300
Atomization (1800 °C)	10	2000
Cleaning (2500 °C)	5	1000

In each step maximum internal gas flow (argon: 0.30 L min^{-1}) was applied.

In modern life, usage of vitamins and the analysis of mineral tablets have increased rapidly. Conventionally, metal contents of vitamin–mineral tablets can be determined by digesting samples with acids and subsequent measurements of elements of interest by different instrumental methods.

The aim of this work was to compare different calibration techniques for the direct determination of Mn content in vitamin–mineral tablets using SS-ETAAS.

2. Experimental

2.1. Apparatus

An Analytik Jena Vario 6 Atomic Absorption Spectrophotometer, equipped with deuterium hollow cathode lamp background correction system, transversely heated graphite furnace and full automatic SSA 61 autosampler for solid samples, was used throughout this study. Hollow cathode lamp (Unicam Analytical Systems) was used as the radiation sources for Mn. Pyrolytically coated graphite tubes (Analytik Jena, Part No. 07-8101225) and pyrolytically coated graphite platforms (Analytik Jena, Part No. 07-8131225), designed for suitable solid sampling, were used for all experiments. Solid sampling tubes are without a dosing hole and open for the solid sampling properly. Samples were introduced into the graphite tube on a special platform designed for solid samples with SSA 61 solid autosampler. Samples which were put on to the platforms were automatically weighed in the microbalance of the sampler precisely at 0.001 mg level and transported into the tube again automatically with its robotic tweezers. To obtain the same heating conditions with solid samples, the solutions were pipetted on to the same platforms of solid autosampler with 10 μl of Eppendorf pipette manually.

Peak areas were applied for quantification. Instrumental and experimental conditions for the determination of Mn in vitamin–mineral tablets are given in Table 1. All samples were powdered before analysis using agate mortar. Typical weights for direct solid sampling were in the 50–300 μg range.

2.2. Reagents

A stock solution containing 1000 mg L^{-1} of manganese as the nitrate was prepared from Titrisol concentrates (Merck). All reagents were of analytical reagent grade (Merck). All working solutions were prepared daily by appropriate dilution of stock solutions with freshly distilled deionized water. Argon (99.99%; Habas Co., Turkey) was used as a purge gas.

2.3. Procedure

The vitamin tablets produced by the manufacturer (Deva Co., Istanbul, Turkey) are sent to our laboratory regularly for each production series for the validation of included elements. Vitamin–mineral tablets consist of two main parts: seed and coating. Seed contains all metals and minerals. For a better homogeneity, only seeds of tablets were used in all experiments. If tablets (seed + coating; on an average 0.6 g per tablet) had been used, the small powdered sample aliquots consisting of seed and coating would have been less homogenous which is an important problem in solid sampling. For this reason determination of metal contents of tablets was investigated using seeds of tablets. At first, the seeds obtained from the producer were ground. For the conventional analysis of samples, 1.45 g of powdered sample (10 seeds) was digested within 15 min using 15 ml of HNO_3+HCl(2+1) mixtures on hot plate at 100 °C. After dilution appropriately, manganese content was determined by AAS. For solid sampling, a part of powdered sample was directly put on the platform of the autosampler. It was weighed and introduced in to the furnace by means of autosampler automatically. Whenever necessary, solutions were pipetted on the same platform by micropipette manually.

3. Results and discussions

In solid sampling AAS, interferences, atomization kinetics, shape of the signals and thus the sensitivity of the analyte change with the amount of sample, particle size, chemical form of the analyte and the composition of the matrix. However the use of stabilized temperature platform furnace (STPF) concept is capable of eliminating almost all the problems associated with atomization kinetics and signal shape. In addition the samples cannot be appropriately and homogeneously diluted when solid sampling technique is used. As long as the sample and the standards do not match with respect to their composition, particle size and chemical form of the analyte element, there is always a risk of error. Because of these drawbacks, one of the most important steps in solid sampling ETAAS is to apply a suitable calibration technique.

3.1. Solution technique

Mineral tablets were dissolved as described in Section 2 and analyzed against aqueous standards by linear calibration

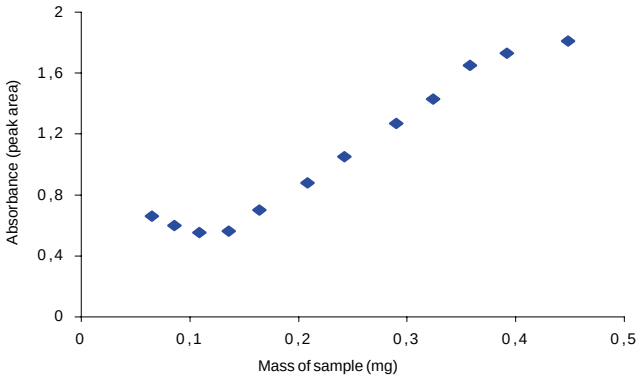

Fig. 1. The effect of sample mass vitamin tablets on the peak area.

to compare the results obtained from solid sampling. After 10 independent determinations (different samples at different dates), Mn contents of vitamin–mineral tablets found against the aqueous standards is $193 \pm 5\,\mathrm{mg\,kg^{-1}}$ (or on an average 0.028 ± 0.0007 mg per tablet assuming that the weights of tablets are equal). The results are exactly in consistent with the values given by the manufacturer of the tablets ($193\,\mathrm{mg\,kg^{-1}}$).

Although the concentration of Mn in the sample is high enough to be determined directly without any enrichment step, the procedure was completed more than 1 h because of digestion step which would not be necessary for solid sampling. If a preconcentration/separation process prior to determination of Mn had been necessary then the whole procedure for one sample would have taken much longer time and errors due to contaminations or analyte losses may be possible.

3.2. Solid sampling

At first, the change of absorbances with the amount of sample introduced into the furnace was investigated. The effect of sample mass on the sensitivity (i.e. peak area per unit sample mass) for vitamin tablets is shown in Fig. 1. As shown in the figure the slope of the curve is constant between 0.15 and 0.4 mg of sample. Sensitivity (absorbance per unit sample mass) increases at lower sample masses, whereas it decreases above 0.4 mg of sample. Since the sample mass cannot be kept constant there would be some errors due to use of different masses of samples out of 0.15–0.4 mg sample range. Same types of data were obtained by Belarra et al. They investigated effect of sample mass on the direct determination of metals in solid samples by graphite furnace atomic absorption spectrometry, and found overestimated and underestimated results when sample mass was small and high, respectively [5,10]. Different explanations were made for the overestimated results obtained from small sample masses which are condensation of volatile elements on particle surfaces [7], inaccurate background correction [8] and water content in the sample [9]. Thus, it is not unusual that absorbance per unit mass of sample changes with sample mass. In this case, the choice of an appropriate calibration technique and working range with respect to sample masses become much more critical steps. Actually, the manganese contents of 0.4 mg of sample (77 ng of Mn) is still in the linear range at 403.1 nm found from standard solution and thus the change of sensitivity cannot be attributed to deviations from linearity of Beer Law.

In addition, since the change of sensitivity is not proportional to sample mass, it is not possible to apply zero matrix extrapolation technique which was proposed in some applications of solid sampling ETAAS [8].

Three different calibration techniques were used for solid sampling and the results were compared with those of solution technique: (i) linear calibration with aqueous standards; (ii) standard addition method with aqueous standards; (iii) calibration against solid CRM.

3.2.1. Linear calibration with aqueous standards

Calibration curve was produced using aqueous standards. The masses of sample introduced to the furnace were 0.150–0.300 mg. These masses correspond to 28.8–58 ng of manganese (or 10 μl of $2.88–5.8\,\mathrm{mg\,L^{-1}}$ Mn) which are too high to be determined at the most sensitive resonance line of 279.5 nm. The possible lines for Mn are 279.8, 280.1 and 403.1 which are 1.4, 2.3 and 9 times less sensitive than the resonance line, respectively. Thus, alternative line of 403.1 nm was used throughout this study.

Effects of pyrolysis temperature and atomization temperature on the absorbance using aqueous standards are shown in Figs. 2 and 3. The pyrolysis and atomization curves for Mn in the samples introduced as solid form are not remarkably different from those for aqueous matrix-free standards with only difference that the optimum atomization temperature for solid samples is 1800 °C which is 1700 °C for aqueous standards.

At optimum experimental conditions for solid sampling, the Mn concentration after 10 independent replicate analysis was found as $198 \pm 10\,\mathrm{mg\,kg^{-1}}$. This value is in the limits of 95% confidence level. In solid sampling technique, only a very small part of whole sample is introduced into the furnace. Because of the inhomogeneous distribution of the analyte, the whole sample cannot be represented with only

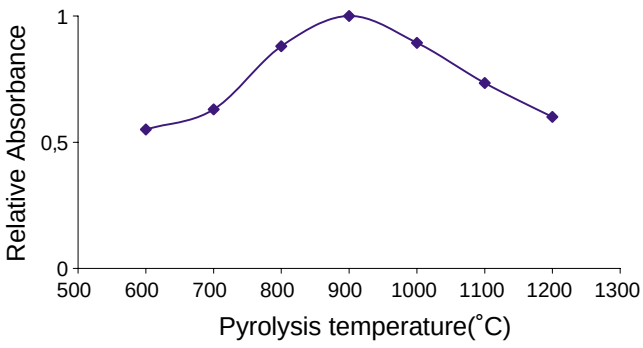

Fig. 2. Effect of pyrolysis temperature on the absorbance.

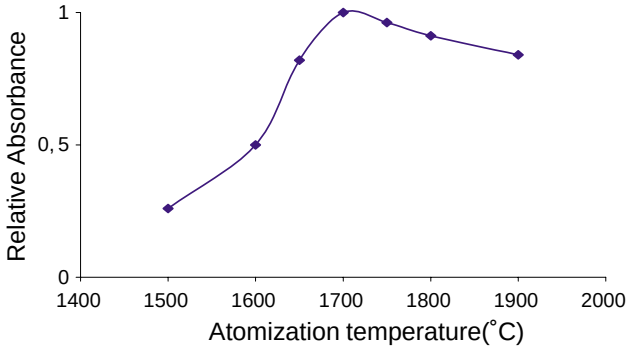

Fig. 3. Effect of atomization temperature on the absorbance.

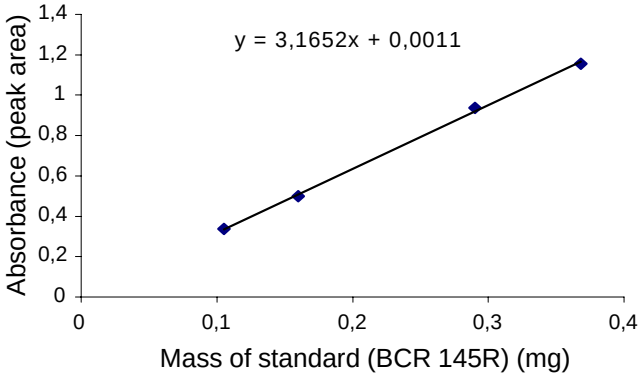

Fig. 4. Calibration curve obtained by using BCR 145R.

one portion of solid sample. Thus, several different portions of sample should be introduced into the furnace for the average of determination to represent the whole sample with satisfactory RSD values. To get reliable results, the number of independent replicates should be higher than that of solution technique.

3.2.2. Standard addition method with aqueous standards

Solid samples were placed on the platform. The mass of sample was automatically weighed and then aqueous standard solutions were added on it before graphite furnace program was operated. In the calibration curve, mass of sample could not be kept constant. In other words, variable concentrations of aqueous standards were added to variable mass of sample. As a result, three-dimensional curve was obtained. Software of the instrument produced a three-dimensional curve and calculated metal concentration of sample as $164 \pm 18\,\mathrm{mg\,kg^{-1}}$ ($N = 8$) irrespective of atomization temperature (whether 1700 or 1800 °C). There is still a real difference between results found by addition of aqueous standard on solid samples and dissolution of sample.

If analyte standard solution was added on the solid sample, the increases in the absorbances are different than expected, i.e. than those observed for matrix-free analyte. The presence of solid sample causes an around 20% depressive interference on the absorbance for analyte introduced as solution. This problem may be originated from unsuitable furnace program and reduced by changing temperature program. This error should be originated from being different phases of standard and sample at the same time. In order to overcome this problem 10 μl of $1\,\mathrm{mg\,L^{-1}}$ Mn standard dried on solid sampling boats and solid samples was fed to the furnace using these boats. In each case mass of added Mn is 10 ng but variable mass of sample was fed to the furnace. In that condition Mn content was found as $185 \pm 15\,\mathrm{mg\,kg^{-1}}$ ($N = 8$). If furnace program has been changed this problem might be solved too.

3.2.3. Calibration with solid CRM

Since the certified solid standard of vitamin tablets are not available, BCR 145R (sewage sludge) was selected as the solid standard. The effect of mass of BCR 145R on the absorbance is shown in Fig. 4. As shown in the figure the absorbance is linearly changed with mass between 0.1 and 0.37 mg of solid sample. Mn content of BCR 145R is $156 \pm 4\,\mathrm{mg\,kg^{-1}}$. Its concentration is close to that of vitamin tablets and the same wavelength can be used for both of them. By using this calibration method Mn content of tablets was found as $201 \pm 8\,\mathrm{mg\,kg^{-1}}$ ($N = 10$). This value is in good agreement with that found by solution technique ($193\,\mathrm{mg\,kg^{-1}}$). The Mn content found against a solid standard (even if the matrix content of solid standard does not match exactly with that of sample) is consistent with those obtained from solution calibration and that added by the producer.

4. Conclusion

Direct solid sampling was successfully applied to the analysis of vitamin–mineral tablets. Analysis carried out with solid standards is also successful even if its matrix is different from that of the sample. After optimization of experimental conditions even with aqueous standards good results could be obtained having all advantages of solid sampling. The drawback of the solid sampling technique such as need for a great number of repetitions due to inhomogeneity of samples is compensated with less effort to prepare the sample to analysis.

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