

**Methods of Sample Thermal Modification by means Double Vaporization in Two Step
Atomizer for Atomic Absorption Analysis.**

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ABSTRACT:

After sample vaporization in two-step atomizer with a purged vaporizer sample vapors can be transferred into preheated or into non-heated atomizer. In the last case the atomizer walls trap the vapors and then the sample is second time vaporized and atomized by heating the atomizer. Thermal pre-treatment of a sample using this double vaporization makes possible the direct analysis of samples with strongly interfering matrices including solids. The technique was used for the direct determination of Cd and Pb in human urine, high concentrated water solutions of NaCl, Na₂SO₄, NaNO₃, KH₂PO₄ and NH₄H₂PO₄ matrices, potatoes, wheat, bovine liver, milk powder, grass-cereals mixture, caprolactam, bituminous-shale and polyvinyl chloride plastic without chemical modification or any other sample pre-treatment.

INTRODUCTION

One of the advantages of electrothermal atomization (ETA) technique is the possibility of thermal sample pretreatment before its vaporization and atomization.

The majority of commercial electrothermal atomizers can be classified as single-step systems, where the same cell is used for both vaporization and atomization of the sample.

Thermal pretreatment in these systems typically includes only drying and pyrolysis [1] of samples.

A two-step atomizer with vaporizer purging (TSAVP) [2 - 4] seems to be suitable to realize additional possibility for sample thermal modification using the idea of double vaporization of the sample [5 - 12]. Two-step atomizers consist of an independently heated vaporizer and an atomizer-cuvette [2 - 4, 13-15]. The vaporizer can be purged by argon jet.

During the double vaporization the sample is first vaporized in the vaporizer, the vapors transported to the cold atomizer-cuvette and trapped inside, and the sample is then re-vaporized into the analytical zone (Fig. 1). Additional sample transformation occurs during sample vaporization. Phosphates, sulfates, nitrates, halides and other constituents of the sample matrix are partly or completely decomposed if the temperature is high enough. Gaseous and volatile decomposition products will not, or at least will not be fully trapped in the atomizer-cuvette. In addition, trapping of non-decomposed matrix on the atomizer surface may be in a different way than for the analyte. This way the actual quantity of matrix vaporized into the analytical zone simultaneously with the analyte is reduced before the final atomization and, as a result, interferences will be reduced.

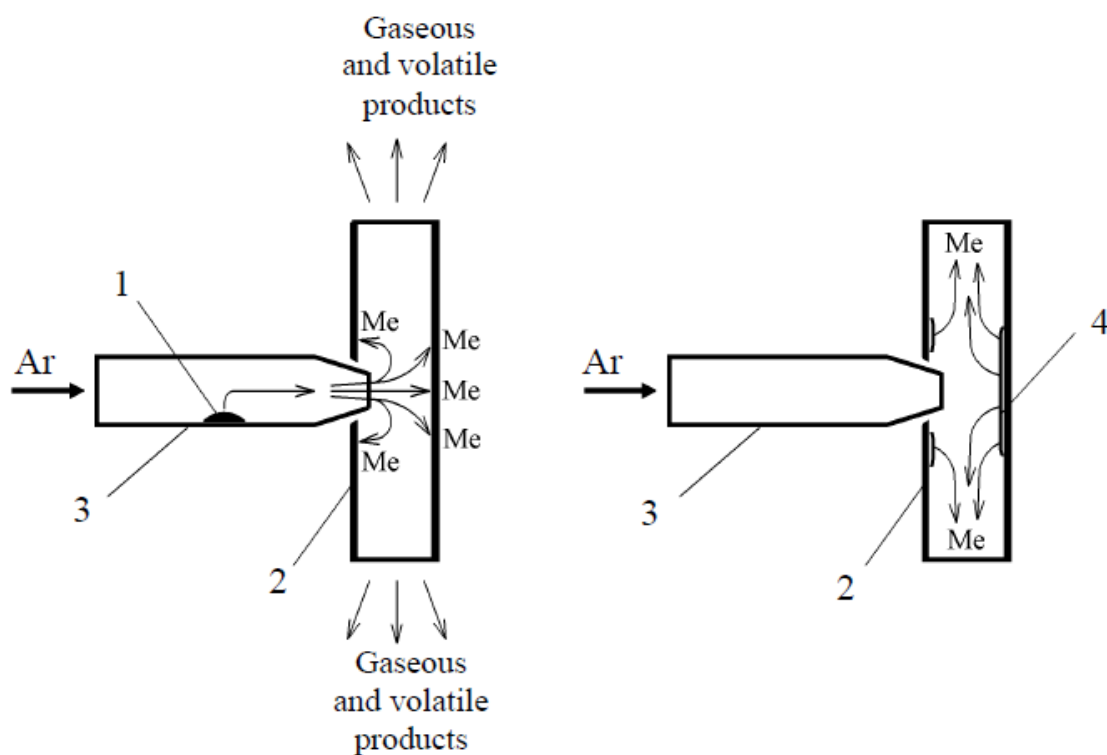


Fig. 1. Principle of double vaporization of the sample using the two-step atomizer. 1 – initial sample; 2 – atomizer-cuvette; 3 – vaporizer; 4 – trapped sample; Me – analyte.

The aim of this work was to investigate the possibility of using the double-vaporization mode of TSAVP for thermal modification of the samples with strongly interfering matrices. Human urine, high concentration water solution of NaCl, Na₂SO₄, NaNO₃, KH₂PO₄ and NH₄H₂PO₄ matrices, potatoes, wheat, bovine liver, milk powder, grass-cereals mixture, caprolactam, bituminous-shale and polyvinyl chloride plastic were selected as samples to be investigated. Pb and Cd were selected as the analytes because it is very difficult for volatile metals to remove the matrix in the pyrolysis step without using modifiers.

EXPERIMENTAL

The two-step atomizer with vaporizer purging used in this work for the analysis of liquid samples has been described previously [4]. The two-step atomizer is placed inside a small argon-purged metal chamber. The dimensions of the main parts of the TSAVP used in this investigation are shown in Fig. 2 (A). For the analysis of solids the system was slightly modified [16]. Two versions of the modified TSAVP were used. In the first one (Fig. 2 (B)) a disk-shaped graphite partition with several holes of 0.3 mm diameter was installed in the vaporizer to prevent the ejection of large non-atomized particles of the sample into the atomizer-cuvette. In the second construction (Fig. 2 (C)) a porous graphite capsule (2 mm inner diameter, 3 mm external diameter, 12 mm long) was used for the sample location in the vaporizer. A boron nitride gasket, which was fixed in a small metallic door in front of the atomizer chamber, was used to prevent the sample vapours to escape from the vaporizer (Fig. 2 (B, C)).

The chamber with the two-step atomizer was placed in the optical axis of atomic absorption spectrometer with deuterium background correction, which was used in all the experiments with the TSAVP.

A Hitachi Z 9000 (Hitachi, Japan) multielement atomic absorption spectrometer with Zeeman-effect background correction, Shimadzu AA-6800 atomic absorption spectrometer with high frequency self-reversed background correction and an AAS-3 (Carl Zeiss Jena, Germany) flame atomic absorption spectrometer were used for some experiments. Standard platform-furnace atomizer was used in the experiments with Shimadzu AA-6800 instrument. A home-made pyrocoated L'vov platform was used with the standard pyrocoated graphite tubes to analyze liquid samples with the Hitachi instrument. A standard cup-tube atomizer with a home-made graphite capsule was used for the analysis of solid samples in the experiments with the Hitachi instrument.

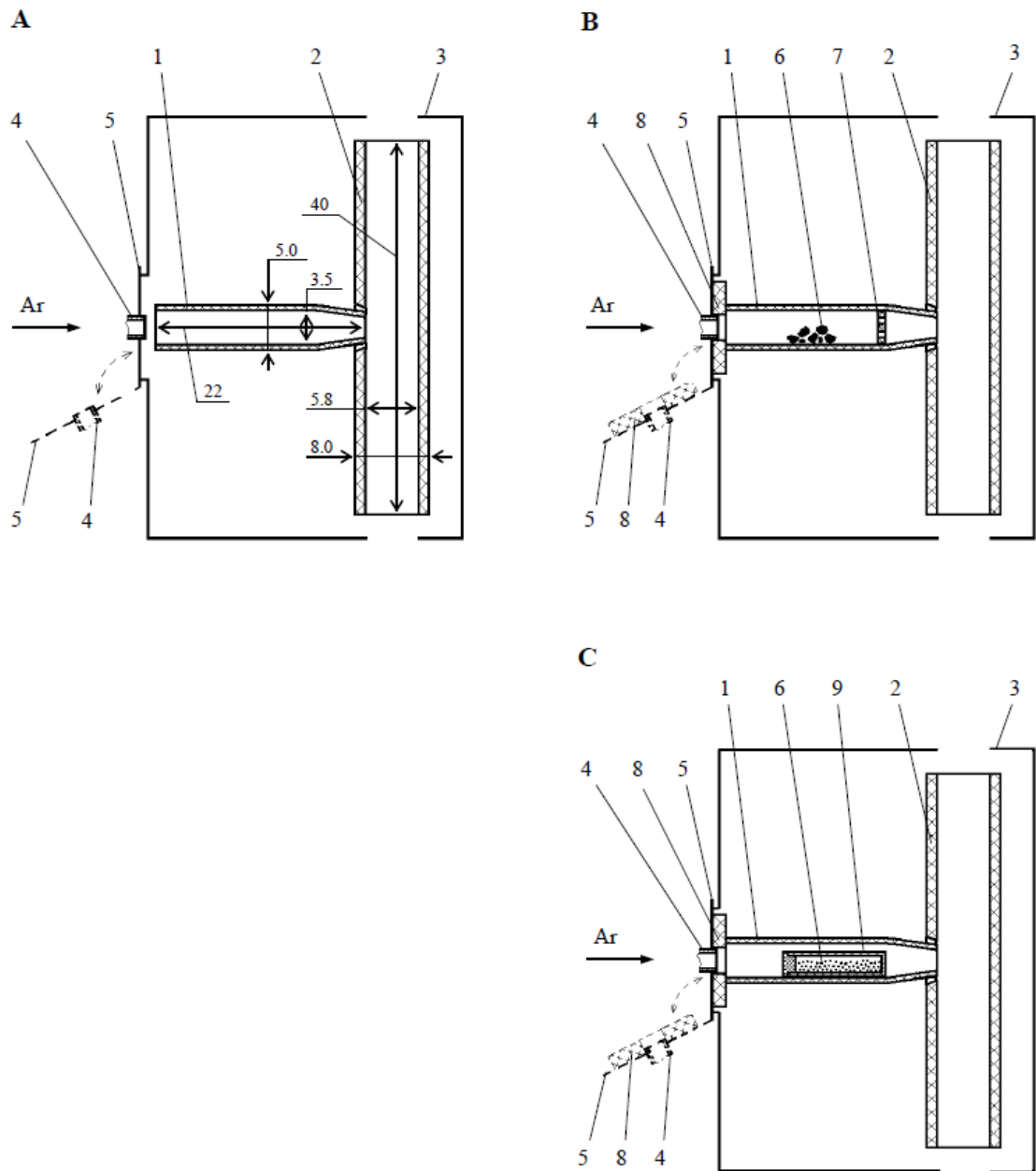


Fig. 2. Different designs of the two-step atomizer with vaporizer purging (A–C) and Hitachi cup-tube atomizer with a home-made graphite capsule (D). A – ordinary TSAVP; B – TSAVP with graphite partition; C – TSAVP with graphite capsule; 1 – vaporizer; 2 – atomizer-cuvette; 3 – atomizer chamber; 4 – connecting pipe; 5 – metallic door; 6 – solid sample; 7 – graphite partition; 8 – boron nitride gasket; 9 – graphite capsule; 10 – Hitachi standard cup-tube atomizer; 11 – graphite capsule. All dimensions are in mm.

Spectrophotometer KFK-3 (ZOMZ, Russia) and ionometer I-120.1 (GZIP, Belorussia) with NO_3^- - selective electrode (VOLTA, Russia) are used for determination of Cl^- , SO_4^{2-} , NO_3^- and PO_4^{3-} correspondingly.

Hollow cathode lamps LT-2 (KORTEK, Russia) and HLA-3 or HLA-4 (Mitorika, Japan) or EDL lamps (KORTEK, Russia) were used.

An optical pyrometer EOP-66 (OZOP, Ukraine) was used for temperature measurements (precision $\pm 10^0$ at 2500^0C).

A chromel-alumel thermocouple was used for low ($<800^0\text{C}$) temperature measurements (precision $\pm 5^0$ at 100^0C).

An analytical micro-balance VLE-20 (GOSMETR, Russia) with a scale division of 0.01 mg was used for weighing the solid samples.

MPG-8 type graphite (NIIGRAFIT, Russia) was used to manufacture all the graphite parts of the TSAVP and of the home-made graphite capsules.

Stock standard solutions were prepared by dissolving metallic Pb and Cd of purity higher than 99.9% in diluted nitric acid.

The following reference samples were used:

- SeronormTM Trace Elements Urine, batch 101021 (NYCOMED PHARMA AS Diagnostics, Norway);
- NIST SRM 1577b Bovine Liver (National Institute of Standard and Technology, USA);
- Russian State Standard Sample (RSSS) SBMK-02 Potatoes (Central Research Institute of Agricultural Chemistry, Russia);
- Russian State Standard Sample (RSSS) SBMP-02 Wheat (Central Research Institute of Agricultural Chemistry, Russia).

Liquid (human urine and water solution of “chemically pure” quality of different salts) and solid (milk powder and grass-cereal mixture) samples, spiked with Cd and Pb, were used in some experiments.

Nitric and sulfuric acids, hydrogen peroxide and dimethylacetamide of “chemically pure” quality and spectral pure graphite powder of OSC-7-4 type were used. High purity argon (99.99%) was used as shielding and transferring gas.

Ten or twenty microliters of sample with known content of investigated matrix is introduced into the vaporizer for determination of reduction degree (γ) of matrix anions or elements contents due to double vaporization procedure. The sample is dried (30 s, 150⁰C). Then the vaporizer with this initial sample is removed out of TSAVP. For the determinations of Cl⁻, SO₄²⁻, NO₃⁻ and PO₄³⁻ anions the vaporizer is exposed 30 min. in boiling (water bath) distilled water. Chloride and sulfate contents are determined using nephelometric method based on reaction with Ag and Ba correspondingly. Ion selective electrode technique is used for nitrate determination. Phosphate is determined using photolorimetry with phosphorus-molibdenum-vanadium complex. Extraction completeness was confirmed comparing the obtained result with known content of the anion in the sample. Then the similar sample is introduced into the vaporizer again. The sample is dried and then vaporizer temperature is increased up to 2000⁰C. The sample vapors are transferred into non-heated atomizer-cuvette with Ar jet. The atomizer-cuvette is removed out of the device and just the same procedure of ion extraction is realized. For total phosphorus determination the vaporizer or the atomizer is crushed in ball-mill. The powder is analyzed using standard optical emission spectrometry procedure. In all the cases γ is determined as ratio of the anion contents measured in the cuvette and in the initial sample.

Ten or twenty microliters of a liquid sample or 0.1 mg to 15 mg of a solid sample were introduced into the vaporizer during atomic absorption measurements. Under the double-vaporization mode, the sample vapors were transported by a flow of argon from the vaporizer into the non-heated atomizer, the wall temperature of which, measured by a thermocouple, did not exceed 100⁰C. The atomizer cuvette was then heated consecutively to the drying, pyrolysis and atomization temperatures, and the atomic absorption peak area was measured. The

platform- or cup-tube atomizers were used in some experiments for comparison with the TSAVP under double-vaporization mode. The temperature programs for Pb and Cd determination in liquid and solid samples, using the TSAVP, are shown in Tables 1 and 2, respectively. During the atomization stage in the double-vaporization mode a small part of the analyte diffuses back to the vaporizer and is trapped on the surface of its tip. A cleaning stage with increased argon flow was used to eliminate this memory effect. During the measurements with Shimadzu and Hitachi platform furnaces the same sample volumes and standard atomization procedures are used. The temperature programs for Pb and Cd determination in solid samples, using Hitachi cup-tube atomizer with graphite capsule, are shown in Table 2. Atomic absorption and background signals are measured in all cases.

Table 1. Temperature programs for Cd and Pb determination in liquid samples, using TSAVP.

Step	Temperature (°C)		Time (s)		Argon flow rate (ml/min)
	Vaporizer	Atomizer	Ramp	Hold	
Drying	200	<100	10	20	0
Pyrolysis	800 (Cd) 400 (Pb)	<100	10	15	100
Vaporization	2000	<100	1	2	100
Drying	<100	200	10	20	0
Pyrolysis	<100	280 (Cd) 400 (Pb)	5	10	100
Atomization	<100	2000	1	4	0
Cleaning	2400	2400	1	2	350

Table 2. Temperature programs for Cd and Pb determination in solid samples.

Atomization technique	Step	Temperature ($^{\circ}\text{C}$)		Time(s)		Argon flow rate (ml/min)
		Vaporizer	Atomizer	Ramp	Hold	
TSAVP, double vaporization	Drying	200	< 100	20	100	0
	Pyrolysis	700	< 100	10	15	350
	Vaporization	2000	< 100	1	4	350
	Drying	< 100	200	10	20	0
	Pyrolysis	< 100	280 (Cd) 400 (Pb)	5	10	100
	Atomization	< 100	2000	1	4	0
	Cleaning	2400	2400	1	2	350
Hitachi cup tube atomizer	Drying	-	150	5	25	100
	Pyrolysis	-	280 (Cd) 400 (Pb)	5	25	100
	Atomization	-	2000	1	5	0
	Cleaning	-	2400	1	2	100

Solid samples were normally introduced into the TSAVP vaporizer using the graphite capsule [17] technique. The solid sample was weighed into the porous graphite capsule, which was then inserted into the vaporizer using tungsten-foil pincers and a special plastic stick to avoid contamination and to fix its position in the vaporizer. The small metallic door with the boron-nitride gasket (Fig. 2 (B, C)) was opened before the introduction of a solid sample and closed afterwards. The graphite capsule technique was also used with the cup-tube atomizer, introducing the graphite capsule through the sampling hole at the bottom of the atomizer (Fig.2 (D)). After the atomization it was removed using special tungsten-foil pincers. In some experiments the TSAVP vaporizer with a graphite partition (Fig.2 (B)) was used for the analysis of solid samples. In this case the pre-weighed sample was directly introduced into the vaporizer using a special tungsten-foil spoon.

The efficiency of analyte transfer and trapping from the vaporizer to the atomizer-cuvette was estimated by introducing an aqueous solution or a graphite powder sample, both with known Cd and Pb content, into the TSAVP vaporizer, and measuring the atomic absorption peak area value (Q) using the double-vaporization mode. An aqueous solution with the same analyte content was then directly introduced into the TSAVP atomizer-cuvette and the atomic absorption peak area value (Q_0) measured using the atomizer-cuvette heating only. The Q/Q_0 ratio was considered as the transfer and trapping efficiency. These experiments have been performed for different analyte concentrations and vaporizer designs.

In all cases aqueous standard solutions of Pb and Cd were used for calibration.

All experiments were performed without any chemical modifier.

The resonance lines for Cd at 228.8 nm and Pb at 283.3 nm were used, unless otherwise noted.

Standard dissolution procedures were used in some experiments for solid samples [1, 18, 19].

RESULTS AND DISCUSSION

The dependencies of the analyte transfer and trapping efficiency on the Ar flow rate through the vaporizer are shown in Fig. 3 for different vaporizer designs. The plots for Cd and Pb are identical. The two-step atomizer with the ordinary vaporizer (Fig. 2 (A)) could be used for liquid samples only, because solid samples caused a high background due to non-atomized particles. The systems with graphite capsule and graphite partition inside the vaporizer could be used for both liquid and solid samples. For all vaporizer types the efficiency of analyte transfer and trapping was approaching 100% for vaporizer purging flow rates above 70 ml/min.

Characteristic mass values 7.3 pg for Pb and 0.4 pg for Cd were obtained for TSAVP which are in a good agreement with the values calculated theoretically by B. L'vov [20] taking into account the longer atomizer-tube used in our experiments.

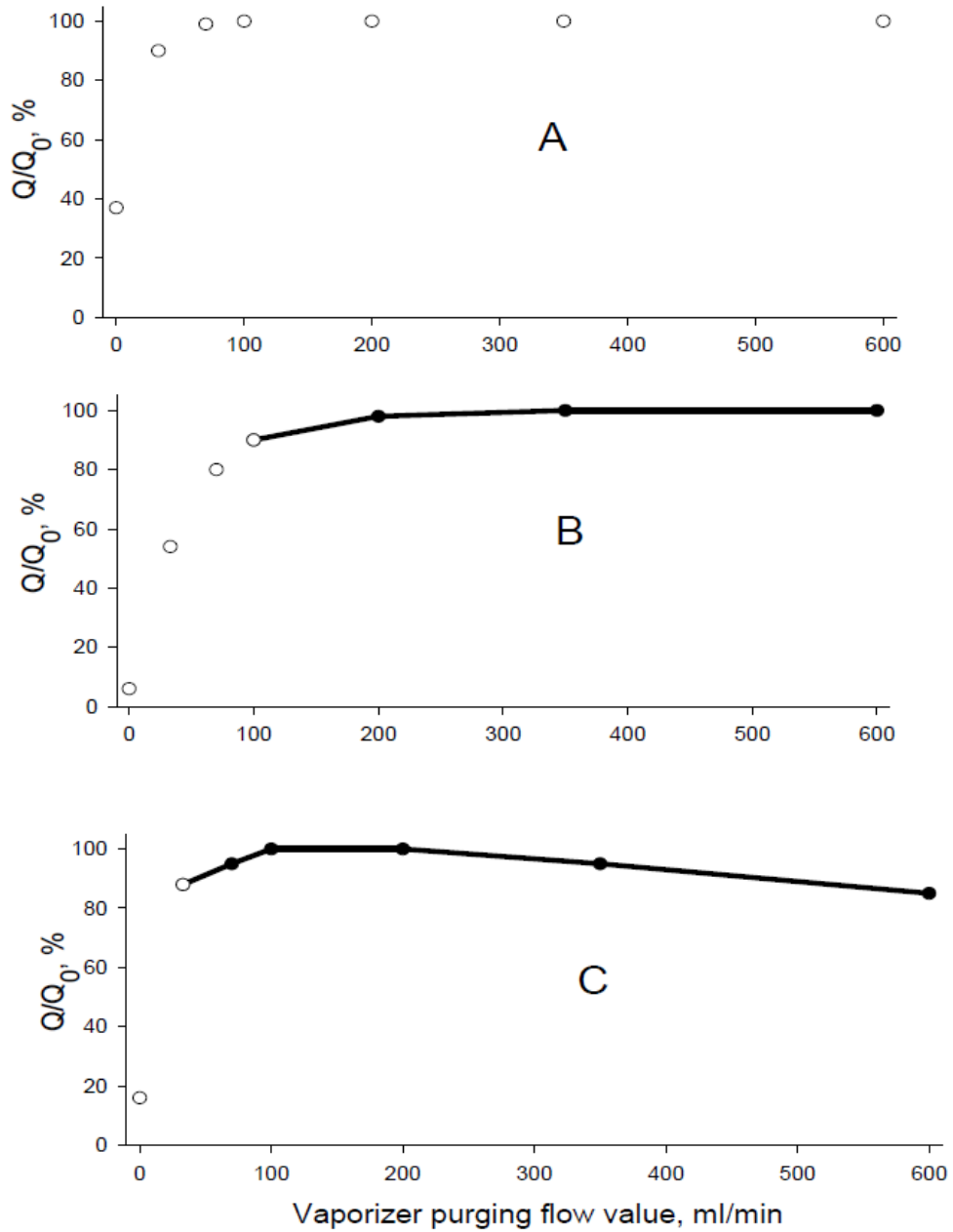


Fig. 3. Dependencies of Cd and Pb transfer and trapping efficiency (Q/Q_0) on the Ar flow rate through the vaporizer for different vaporizer designs. A – ordinary vaporizer; B – vaporizer with graphite capsule; C – vaporizer with graphite partition. Solid line – for both liquid and solid samples; dotted line – for liquid samples only.

The results of anion and phosphorus content determinations in the initial sample and in the sample transferred into the atomizer-cuvette of TSAVP are demonstrated in Table 3 for different matrices. For all investigated matrices these contents are significantly (3-20-fold) reduced after sample vaporization and transferring to the atomizer-cuvette. This confirms the assumption of the authors about additional sample thermal modification during double vaporization in TSAVP. Reduction of matrix anions or elements concentration leads to reduction of background.

Table 3. Reduction of matrix anion contents during sample vaporization inside TSAVP vaporizer and transferring into atomizer-cuvette.

Matrix	Anion to be determined	Known content, μg^*	Measured content, μg		γ
			Vaporizer	Atomizer	
NaCl	Cl^-	115	110 ± 5	20 ± 3	5.5
Na_2SO_4	SO_4^{2-}	270	265 ± 5	20 ± 5	13.2
NaNO_3	NO_3^-	740	760 ± 40	69 ± 6	11.0
KH_2PO_4	PO_4^{3-}	850	860 ± 20	45 ± 3	19.1
	P	2200	2100 ± 300	500 ± 100	4.2
$\text{NH}_4\text{H}_2\text{PO}_4$	PO_4^{3-}	800	800 ± 20	40 ± 3	20.0
	P	2100	2100 ± 300	500 ± 100	4.2
Urine	Cl^{**}	110	110 ± 10	20 ± 5	5.5

* - Accounted for anion; ** - Anion concentration was preliminary measured in sample solution.

In Table 4 background values obtained during double vaporization in TSAVP and during direct atomization in the atomizer-cuvette of TSAVP are compared.

So significant matrix content reduction and background reduction make double vaporization technique promising for the analysis of the samples produced high background signals during atomization.

Table 4. Background values obtained during double vaporization in TSAVP and during direct wall atomization in the atomizer-cuvette. $\lambda = 228.8$ nm.

Matrix	Matrix concentration, %	Background value	
		TSAVP, double vaporization	TSAVP, atomizer-cuvette wall atomization
NaCl	0.1	0.09	0.7
	0.3	0.2	> 1
Na ₂ SO ₄	0.5	0.1	0.85
	2.0	0.35	> 1
KH ₂ PO ₄	0.1	0.19	0.45
	0.2	0.37	0.88
NH ₄ H ₂ PO ₄	0.5	0.07	0.27
	1.0	0.12	0.52
Urine	100	0.25	> 1

Background and recovery values obtained during Cd and Pb determination in different water solution salts and different urine samples using different atomization techniques are demonstrated in Tables 5-7. The background values for the investigated samples, when using the double-vaporization TSAVP technique were 1.5 – 10 lower than those obtained for the Hitachi and Shimadzu platform furnaces. This background reduction makes it possible to use simple deuterium background correction for the analysis. For all the investigated samples the recovery values obtained using double vaporization with TSAVP were approximating 100%, whereas for the Shimadzu and Hitachi platform furnaces recovery values were in some cases significantly worse.

Table 5. Background and recovery values obtained during determination of 10 pg of Cd* in different matrixes using different atomization techniques. $\lambda = 228.8$ nm.

Matrix	TSAVP, double vaporization		Hitachi platform furnace	
	BG	R**, %	BG	R**, %
NaCl, 0.10 %	0.09	100	1.1	90
NaCl, 0.25 %	0.20	100	2.2	-***
Na ₂ SO ₄ , 2 %	0.35	100	0.42	100
KH ₂ PO ₄ , 0.2 %	0.35	100	0.75	100
KH ₂ PO ₄ , 0.5 %	0.90	-***	1.9	-***
NH ₄ H ₂ PO ₄ , 1 %	0.12	100	0.35	100

*- Characteristic masses for Cd is 0.8 pg using Hitachi platform furnace;

$$** - R = \frac{\text{Found content in spiked sample} - \text{Found content in initial sample}}{\text{Added content}} \times 100\% [21];$$

*** - Background signal can not be compensated.

Table 6. Background and recovery values obtained during determination of 250 pg of Pb* in different matrixes using different atomization techniques. $\lambda = 283.3$ nm.

Matrix	TSAVP, double vaporization		Hitachi platform furnace	
	BG	R**, %	BG	R**, %
NaCl, 0.25 %	0.15	100	0.42	73
NaCl, 0.50 %	0.28	100	0.85	60
Na ₂ SO ₄ , 0.50 %	0.05	100	0.24	60
Na ₂ SO ₄ , 1.0 %	0.10	96	0.50	55

*- Characteristic masses for Pb is 15 pg using Hitachi platform furnace;

$$** - R = \frac{\text{Found content in spiked sample} - \text{Found content in initial sample}}{\text{Added content}} \times 100\% [21]$$

Table 7. Background (BG) and recovery values (R,%)* obtained during Cd (228.8 nm) and Pb (283.3 nm) determination in natural urine spiked samples with 1.0 ppb of Cd and 10 ppb of Pb and in Seronorm™ Trace Elements Urine (batch 101021) reference sample with 0.35 ppb of Cd and 3.0 ppb of Pb.

Sample	Element	TSAVP, double vaporization		Hitachi platform furnace		Shimadzu platform furnace	
		BG	R,%	BG	R,%	BG	R,%
Spiked samples	Cd	0.3	96±5	0.4	136±4	0.4	100±4
	Pb	0.1	103±4	0.6	80±10	-	-
Reference sample	Cd	0.2	103±5	0.2	89±20	0.3	120±5
	Pb	0.05	104±6	0.4	63±7		

$$* - R = \frac{\text{Found content in spiked sample} - \text{Found content in initial sample}}{\text{Added content}} \times 100\% \text{ for}$$

$$\text{spiked samples and } R = \frac{\text{Found concentration}}{\text{Known concentration}} \times 100\% \text{ for reference sample [21].}$$

The results of the direct analysis of solid samples using the double-vaporization mode of the TSAVP and the cup-tube atomizer with a graphite capsule (Fig. 2 (D)) are shown in Tables 8 and 9. The TSAVP with graphite partition was used for Cd determination in potato sample and the TSAVP with graphite capsule for all the other samples. The sample mass used in these experiments was typically 0.1 - 1 mg, except for caprolactam, where 2.5 – 15 mg were used. The background values for samples with similar mass, when using the double-vaporization TSAVP technique were 2.3 – 4.7 times lower than those obtained for the cup-tube with graphite capsule (Table 8). This background reduction makes it possible to use simple deuterium background correction for the analysis.

Table 8. Background values (BG) obtained during direct Cd and Pb determination in solid samples using TSAVP and Hitachi cup-tube atomizer with graphite capsule

Sample	Element	TSAVP		Hitachi cup-tube	
		Sample mass (mg)	BG	Sample mass (mg)	BG
Powder milk	Cd	0.30	0.35	0.29	1.2
	Pb	0.31	0.12	0.30	0.36
Grass-cereals mixture	Cd	0.52	0.3	0.55	1.4
	Pb	0.50	0.1	0.49	0.25
RSSS SMBK-02 Potatoes	Cd	0.48	0.12	0.51	0.5
	Pb	0.49	0.05	0.50	0.12
RSSS SMBP-02 Wheat	Pb	0.63	0.1	0.68	0.25
SRM 1577b Bovine liver	Cd	0.41	0.2	0.38	0.6
	Pb	0.72	0.3	0.78	0.68

For all the investigated samples the recovery values obtained using double vaporization with TSAVP were approximating 100%, whereas for the cup-tube technique with graphite capsule recovery values were significantly worse for the majority of the samples investigated (Tables 9 and 10).

Table 9. Result of direct determination of Pb and Cd in solid samples spiked with 20 pg of Cd and 500 pg of Pb and recovery values (R) obtained using Hitachi cup-tube atomizer and TSAVP with graphite capsule.

Sample	Sample mass (mg)	Element	TSAVP			Hitachi cup-tube		
			Found content (pg)		R* (%)	Found content (pg)		R* (%)
			Initial sample	Spiked sample		Initial sample	Spiked sample	
Powder milk	0.3	Cd	2.9 ± 0.5	24 ± 4	105	<1.0	11.6 ± 2	58
		Pb	85 ± 14	590 ± 80	101	56 ± 10	428 ± 70	74
Grass-cereals mixture	0.5	Cd	31 ± 4	50.5 ± 7	98	38 ± 5	51 ± 7	65
		Pb	345 ± 45	880 ± 100	107	310 ± 40	790 ± 90	96

$$* - R = \frac{\text{Found content in spiked sample} - \text{Found content in initial sample}}{\text{Added content}} \times 100\% [21].$$

Table 10. Results of direct determination of Pb and Cd in solid reference samples and recovery values (R) obtained using Hitachi cup-tube atomizer and TSAVP with graphite capsule or filter.

Sample	Element	Known concentration ($\mu\text{g}/\text{kg}$)	TSAVP		Hitachi cup-tube	
			Found concentration ($\mu\text{g}/\text{kg}$)	R* (%)	Found concentration ($\mu\text{g}/\text{kg}$)	R* (%)
RSSS	Cd	120 ± 20	135 ± 20	112	72 ± 10	60
SMBK-02 Potatoes	Pb	200 ± 40	202 ± 30	101	200 ± 30	100
RSSS SMBP-02 Wheat	Pb	190 ± 40	203 ± 26	107	152 ± 20	80
SRM 1577b	Cd	500 ± 14	512 ± 89	102	490 ± 90	98
Bovine liver	Pb	129 ± 4	133 ± 9	103	117 ± 20	90

$$* R = \frac{\text{Found concentration}}{\text{Known concentration}} \times 100\% [21].$$

For several solid samples the results of direct Cd and Pb determinations using the double-vaporization TSAVP technique with graphite capsule were in a good agreement with the results obtained using the TSAVP in its ordinary mode [4] or with other atomization techniques after sample dissolution (Table 11). In order to reduce the sensitivity, an argon flow rate of 350 ml/min was used in the TSAVP atomization stage for Pb determination in bituminous-shale.

Table 11. Results of Pb and Cd determination in different solid samples obtained directly using TSAVP and after the samples pretreatment using different types of atomizers.

Sample	Element	Results of metal determination ($\mu\text{g}/\text{kg}$)	
		TSAVP, directly, double vaporization	After sample pretreatment and dissolving
Wheat	Cd	47 ± 10	$50 \pm 15^*$
Caprolactam	Pb	49 ± 4	$52 \pm 5^{**}$
Bituminous-shale	Pb	24000 ± 2000	$26000 \pm 4000^{***}$
	Cd	22 ± 2	$20 \pm 2^*$
Polyvinyl chloride plastic	Pb****	48000000 ± 5000000	$50000000 \pm 5000000^{**}$

* - Hitachi platform-furnace; ** - TSAVP, ordinary mode; *** - Carl Zeiss AAS-3, flame; **** - 261.4 nm Pb line.

All these results confirm that the double vaporization in TSAVP may be used as a technique for sample thermal modification and that the use of this technique makes possible to reduce interferences during the analysis of the samples with strongly interfering matrices.

CONCLUSION

The double-vaporization mode of the TSAVP may be efficiently used as a technique for thermal modification of liquid and solid samples in order to reduce interferences and to improve the accuracy of results obtained in the analysis of samples with strongly interfering matrix.

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REFERENCES

- [1] B.Welz and M.Sperling, Atomic absorption spectrometry, WILEY-VCH Verlag GmbH, Weinheim, Germany, 1999.
- [2] D. Katskov, V. Kopeikin, I. Grinshtein and I. Burtseva, Zh. Prikl. Spektrosk., 38 682-8 (1983).
- [3] I. Grinshtein, Yu. Vil'pan, V. Kopeikin, L. Vasilieva and M. Meshalkin, "Two-step electrothermal atomizer with a vaporizer purge", in Modern aspects of analytical chemistry, eds. H.-M. Kuss and U. Telgheder, pp. 88-107, Verlag Mainz, Aachen, 1997.
- [4] I. Grinshtein, Yu. Vil'pan, L. Vasilieva and V. Kopeikin, Spectrochim. Acta, Part B, 54, 745-52 (1999).
- [5] T. Mahmood and K. Jackson, Spectrochim. Acta, Part B, 51, 1155-62 (1996).
- [6] G. Chen and K. Jackson, Spectrochim. Acta, Part B, 53, 981-91 (1998).
- [7] D. Katskov and I. Grinshtein, Zh. Prikl. Spektrosk., 28, 968-74 (1978).
- [8] P.Hocquellet, Spectrochim. Acta, Part B, 47, 719-29 (1992).
- [9] T. Rettberg and J. Holcombe, Spectrochim. Acta, Part B, 39, 249-60 (1984).
- [10] T. Rettberg and J. Holcombe, Spectrochim. Acta, Part B, 41, 377-89 (1986).
- [11] T. Rettberg and J. Holcombe, Anal. Chem., 60, 600-5 (1988).

- [12] T. Rettberg and J. Holcombe, *Anal. Chem.*, 58, 1462-7 (1986).
- [13] W. Frech and S. Jonsson, *Spectrochim. Acta, Part B*, 37, 1021-8 (1982).
- [14] W. Frech, A. Cedergren, E. Lundberg and D. Siemer, *Spectrochim. Acta, Part B*, 38, 1435-46 (1983).
- [15] E. Lundberg, W. Frech, D. Baxter and A. Cedergren, *Spectrochim. Acta, Part B*, 43, 451-7 (1988).
- [16] I. Grinshtein, Yu. Vil'pan, A. Saraev and L. Vasilieva, *Spectrochim. Acta, Part B*, (in press).
- [17] D. Katskov, I. Grinshtein and L. Kruglikova, *Zh. Prikl. Spektrosk.*, 36, 536-9 (1980).
- [18] I. Havezov and D. Tsalev, "Atomic absorption analysis", "Himia", Leningrad, 1983.
- [19] V. Price, "Analytical Atomic Absorption Spectrometry", "MIR", Moscow, 1976.
- [20] B. L'vov, *Spectrochim. Acta, Part B*, 45, 633-55 (1990).
- [21] "Interdivisional working party on harmonization. Harmonized guidelines for the use of recovery information in analytical measurement" (Technical Report). IUPAC, *Pure Appl. Chem.*, 71, 337-48 (1999).