

PROBLEMS IN APPLICATION OF ATOMIC ABSORPTION SPECTROMETRY FOR CONTROL OF HEAVY METALS IN TOOTHPASTE

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ABSTRACT

A method for preliminary chemical preparation of toothpaste has been worked out with the aim of a following atomic absorption determination of heavy metals in it. An evaluation of the present standard method for sample preparation of toothpaste has been made, resulting in the conclusion that the use of the method upheld by BSS 15784–83 is unacceptable for a correct determination of some heavy metals. When it is applied, a greater part of the determined elements is captured in the sediment and, if one were to judge only on their contents in the prepared solutions, one could reach the wrong conclusion that the toothpaste complied to the sanitary standard. The proposed method ensures a quantitative transition of the analyzed heavy metals in the solution and a more pronounced destruction of the organic substance. This is achieved in general through preliminary treatment of the analyzed sample with concentrated HNO_3 and a subsequent fusion in a temperature–regulated furnace at 800°C . It has been determined that the degree of extraction of Cu, Cr and Ni in the supernatant is 100 %. The degree of extraction of Pb (98.7%) is acceptable, as is partly the one of Mn (92,2%). The only one to improve on is Zn, which remains captured in a considerable degree in the separated sediment.

Keywords: atomic absorption, heavy metals, toothpaste, preliminary preparation, dry mineralization, destruction of organic substance.

INTRODUCTION

According to Regulation # 34 from 01.09.1995 of the Bulgarian Ministry of Healthcare for the hygiene requirements towards cosmetic substances, analytical control of a series of toxic elements in detergents and toothpaste is required. The regulation sets the maximum allowable quantities of As (1mg/kg), Mn (15 mg/kg), and Cu (50 mg/kg), while completely forbidding the mere existence of traces of Cd, Hg and Bi. According to the existing West-European standard for the contents of heavy metals in toothpaste [4] their highest concentrations have to be in agreement with the limits set in the national laws and standards. In all cases,

however, the prevailing concentration of heavy metals in toothpaste should not be above 20 mg/kg. These strict sanitary regulations on the one hand, and the complex chemical composition of toothpaste on the other, require the use of highly sensitive methods of analysis, which are also with distinct selectivity. The existing scientific literature is not abundant in methods for controlling the amount of heavy metals in toothpaste. Bulgarian State Standard (BSS for short) envisages the employment of a polarographic method for the determination of Pb and Cu (arbitrage), a spectrophotometric one (for Cu). The national pharmacopoeia recommends spectrophotometric method – for As (after its reduction to AsH_3 [1]).

Atomic emission spectrometry in inductively coupled plasma has been suggested for determination of Cu, Pb, Cd, Hg and As [2]. Yet, the fact that toothpastes, which are disperse systems with complex chemical composition, and a difficult object for analysis, should not be neglected. In addition to the inorganic substances, they contain a variety of organic constituents, such as glycerine, sodium dodecylsulphate, Na-carboxymethylcellulose, aerosyl, succharine, formalyne, mint composition, etc., which create serious problems for the sample preparation.

It is known that atomic absorption methods are preferred for control of heavy metals in different objects. The high sensitivity of the determinations, combined at the same time with high selectivity, explain the interest in them. Their application in determination of the heavy metals in toothpaste requires a cautionary choice of the method for preliminary chemical preparation of the analysis samples in accordance with their complex composition. Such an approach is necessary despite the type of the analytic method used—spectrophotometric, spectrographic or polarographic, since, to a great extent, the reliability of the analytic results depends on the correct preparation of the solutions for analysis. The last one envisions the complete destruction of the organic substances, which is accomplished through thermal treatment (dry mineralization) or a treatment with several acids during heating on a sand bath. Unfortunately, the information relating to the chemical preparation of toothpaste is scarce in the scientific literature.

BSS recommends a method for dry mineralization of the samples through fusion in a temperature-regulated furnace at 450 °C for the determination of Pb and Cu. In order to avoid the thermal treatment, some authors [2] favor dissolution of the samples in 12M HCl while weakly heating around 50 °C.

In our opinion, though, such the approach is unacceptable due to the risk of incomplete extraction of the toxic elements contained in toothpaste.

The aim of the present work is an evaluation of the standard method for sample preparation of toothpaste with the subsequent atomic-absorption determination of heavy metals in them.

EXPERIMENTAL

Instrumentation:

An atomic-absorption spectrometer “Perkin—Elmer” –5000 with a deuterium corrector and hollow cathode lamps for Pb, Zn, Cr, Ni, Cu, and Mn as sources of monochromatic light.

A temperature regulated furnace type “LM 211,11”

X-ray diffraction-meter “TUR—M 62”.

Reagents:

37 % HCl; 65 % HNO₃ and 30 % H₂O₂ in qualification p.a. purity.

Standard solutions of Pb, Zn, Cr, Ni, Cu, and Mn (1.00 mg/cm³ BDH Chemicals Ltd)

The investigations have been carried out with the toothpastes “Frech Troya” and “Puro Dent.”

Sample Preparation of Toothpaste (according to BSS 15784–83):

A sample of 5 g (± 0.0002 g), measured in a porcelain crucible is heated on a plate until the emission of vapors ceases. After that a fusion in a temperature regulated furnace at 450 °C for three hours was carried out. If that the obtained residue is not white in color, it is treated with several drops of H₂O₂ and is fused again.

After the mineralization, the residue is carefully treated with 10 cm³ 16 % HCl while slightly heated. After cooling down, the solution is filtered in a 25.0 cm³ volume, and distilled water is added up to the mark of the flask.

RESULTS AND DISCUSSION

In the solutions prepared according to [3] the contents of Pb, Zn, Cr, Ni, Cu, and Mn were determined by flame atomic-absorption spectrometry at conditions, shown in Table 1.

Due to the high volatility of the compounds of As and Hg, the above cited method for preliminary chemical treatment of the analysis samples is not appropriate in the determination of these elements. During the dry mineralization at 450 °C, no significant volatility of the compounds of Cd [2] was discovered, although in the analyzed samples no traces of this ele-

Table 1. Optimal conditions for atomic — absorption determination of Pb, Zn, Cr, Ni, and Mn in flame C₂H₂ (air - 21.4 l/min).

Element	Wave length [nm]	Slit width of [nm]	BG	Acetylene flow rate [l/min]	Height above burner head [mm]	Interval of linearity [$\mu\text{g}/\text{cm}^3$]
Pb	283.3	0.7	OK	2.1	9	2 - 10
Zn	213.9	0.7	OK	2.1	9	0.2 - 1.0
Cr	357.9	0.2	NO	3.3	9	1 - 5
Ni	232.0	0.2	OK	2.1	9	1 - 5
Cu	324.7	0.7	NO	2.1	14	1 - 5
Mn	279.5	0.2	NO	3.0	9	1 - 5

Table 2. Atomic—absorption determination of Pb, Zn, Cr, Ni, Cu and Mn in toothpaste “Puro-Dent “ when the preparation of the samples has been carried out according to BSS 15784-83.

Element	Amount [mg / kg]	Relative standard deviation
Pb	1.35 ± 0.04	2.9
Zn	1.45 ± 0.06	4.1
Cr	2.00 ± 0.05	2.5
Ni	1.40 ± 0.01	0.7
Cu	2.30 ± 0.02	0.8
Mn	3.70 ± 0.02	0.5

* Number of parallel determinations - 5.

ment were observed. The results from the determinations of the above-mentioned elements are presented in Table 2. They are obtained from five parallel samples and an empty sample, prepared analogously.

From the data presented, one could observe that the determinations have distinct reducibility. In our opinion, however, the application of the discussed method, standardized in 1983 for preliminary chemical preparation of the samples is unacceptable, especially when one bears in mind the extremely complex composition of the currently produced toothpastes. An additional reason for such a conclusion is found in the concrete observations in the process of preparation of the samples for analysis. It is evident that there is no complete destruction of the organic constituents. The dry residue after the fusion is dark gray and remains such even after the treatment with H₂O₂ and the subsequent fusion, recommended by BSS in similar cases. Furthermore, after the addition of diluted HCl, a large volume of mass difficult to filter is obtained. This has a pro-

nounced slowing down effect on the process of filtration. The most unpleasant fact is that the quantitative rinsing of the residue is out of question, having in mind its amount on the one hand, and the limited possibility for multiple rinsing on the other (the filtrate and the rinsing waters are gathered in a measurement flask with 25.0 cm³ volume). The danger of systematic underestimation of the analytic results is eminent. This was proved as the content of Pb, Zn, Cr, Ni, Cu, and Mn was determined in the residue isolated on the filter.

The preparation of the sample was carried out in the following manner:

After drying out of the residue at 105 °C and fine grinding down, 0.5 g (0.0002g) of it are measured in a platinum tigel and mixed with 4.0 g. NaCO₃. The sample is fused for 30 min in a temperature—regulated furnace at 1000 °C. After cooling down, the melt is dissolved into 200 cm³ concentrated HCl while heated with a water bath. After several evaporations to “humid salts,” the sample is filtered at high temperature

Table 3. Atomic—absorption determination of Pb, Zn, Cr, Ni, Cu and Mn in toothpaste “Puro—Dent “ in a solution prepared according to BSS 15784 – 83 and the released sediment.

Element	Quantity passed in the solution [mg / kg]	Quantity captured in the sediment [mg / kg]	Total quantity [mg / kg]	Quantity carried by the solution [%]	Quantity captured in the sediment [%]
Pb	1.3	6.3	7.6	17.1	82.9
Zn	1.4	15.8	17.2	8.1	91.9
Cr	2.0	2.6	4.6	43.5	56.5
Ni	1.4	2.3	3.7	37.8	62.2
Cu	2.3	3.0	5.3	43.4	56.6
Mn	3.7	2.3	6.0	61.7	38.3

Table 4. Atomic—absorption determination of Pb, Zn, Cr, Ni, Cu and Mn in toothpaste “Puro—Dent “ after preliminary twofold treatment of the sample with 2 cm³ conc. HNO₃ and subsequent fusion at 450°C.

Element	Quantity passed in the solution [mg / kg]	Quantity captured in the sediment [mg / kg]	Total quantity [mg / kg]	Quantity carried by the solution [%]	Quantity captured in the sediment [%]
Pb	1.7	6.1	7.8	21.8	78.2
Zn	3.1	13.9	17.0	18.2	81.8
Cr	2.5	2.0	4.5	55.6	44.4
Ni	1.4	2.7	4.1	34.1	65.9
Cu	2.4	3.0	5.4	44.4	55.6
Mn	3.9	2.3	6.2	62.9	37.1

through a filter with miniscule particles in a 250cm³ measurement flask.

The results from the determination of the above mentioned elements in a solution prepared according to [1] and the isolated residue of the sample of the toothpaste brand “Puro Dent” are shown in Table 3.

It is clear that when the methodology [1] is employed to chemically prepare the samples, a greater part of the determined elements is captured on the residue. If one were to judge only from their contents in the prepared solutions, one could reach the wrong conclusion that the manufactured toothpaste complies with the sanitary standard. For example, the amount of Pb observed is 1.3 mg/kg, while in reality it is as high as 7.63 mg/kg, which far exceeds the minimum allowable amount of Pb (5 mg/kg).

This necessitates the development of a method for chemical preparation of the samples of toothpaste,

which ensures quantitative transition of the analyzed heavy metals into the solution. Otherwise, the determination of the appropriate elements becomes mandatory in the sediment released after the filtration, which complicates significantly the agenda of the analysis.

It is evident that no complete destruction of the organic substance is accomplished through methodology [1]. To facilitate this process, a treatment of the analysis sample with conc. HNO₃ was performed prior to the fusion in the temperature-regulated furnace.

Ten grams (0.0002 g) of the analyzed sample, measured in a porcelain crucible with 70 cm³ volume, are heated cautiously on a sand bath until the secretion of vapors ceases. After that 2.0 cm³ conc. HNO₃ is added and heated up again until the nitrogen oxides stop vaporizing. The procedure is repeated with a new portion of concentrated HNO₃. Afterwards, the crucible is introduced into a cold furnace and the temperature is gradu-

Table 5. Atomic—absorption determination of Pb, Zn, Cr, Ni, Cu and Mn in toothpaste “Puro—Dent “ after preliminary twofold treatment of the sample with 4 cm³ conc. HNO₃ and subsequent fusion at 450°C.

Element	Quantity passed in the solution [mg / kg]	Quantity captured in the sediment [mg / kg]	Total quantity [mg / kg]	Quantity carried by the solution [%]	Quantity captured in the sediment [%]
Pb	3.8	4.0	7.8	48.7	51.3
Zn	4.5	12.8	17.3	26.0	74.0
Cr	3.0	1.5	4.5	66.7	33.3
Ni	1.5	2.0	3.5	42.9	57.1
Cu	2.5	2.5	5.0	50.0	50.0
Mn	4.9	1.3	6.2	79.0	21.0

Table 6. Atomic—absorption determination of Pb, Zn, Cr, Ni, Cu and Mn in toothpaste “Puro—Dent “ after preliminary twofold treatment of the sample with 8 cm³ conc. HNO₃ and subsequent fusion at 800°C.

Element	Quantity passed in the solution [mg / kg]	Quantity captured in the sediment [mg / kg]	Total quantity [mg / kg]	Quantity carried by the solution [%]	Quantity captured in the sediment [%]
Pb	7.4	0.1	7.5	98.7	1.3
Zn	7.8	10.0	17.8	43.8	56.2
Cr	4.4	-	4.4	100.0	-
Ni	3.5	-	3.5	100.0	-
Cu	5.2	-	5.2	100.0	-
Mn	5.9	0.5	6.4	92.2	7.8

ally increased up to 400 °C at a speed of 100°C/hour. The heating at the specified temperature is carried out for three hours. The dry residue obtained, after cooling down, is dissolved into 10 cm³ HNO₃ (1 : 1), carefully letting it smoke away on a sand bath to dry. The procedure is repeated. To the obtained ashy residue are added 20.0 cm³ hot distilled water, made acidic by adding several drops of HNO₃, and the mixture is filtered into a 50.0 cm³ measurement flask with volume. After subsequent rinsing of the crucible and the sediment in the filter and cooling down, distilled water, acidified with HNO₃, is added to the solution until the mark of the measurement flask is reached. The sediment separated on the filter is dried up at 105 °C and is treated as the discussed above.

In the filtrate and the solution after alkaline melting of the sediment, the atomic-absorption contents of Pb, Zn, Cr, Ni, Cu, and Mn were determined. The results are presented in Table 4.

From the data it is seen that the total amount of the determined elements that have passed into the filtrate has slightly increased, but it is still far from the needed amount for their quantitative determination. The predominant part is still captured in the sediment. It is clear, however, that the preliminary treatment of the toothpaste with conc. HNO₃ has a positive impact. Hence, the amount of HNO₃ for preliminary treatment was increased from 2 to 4 cm³ and the analysis sample was prepared as discussed earlier. The results for the determination of Pb, Zn, Cr, Ni, Cu, and Mn in the filtrate and the sediment are shown in Table 5.

The preliminary treatment of the toothpaste with conc. HNO₃ undoubtedly enhances the destruction of the organic substances. Yet, the ashy residue is still grayish, and a considerable part of the determined elements in the toothpaste is still traceable in the sediment after filtering, as seen from the data presented. It is evident that fusion at 450 °C does not reach the de-

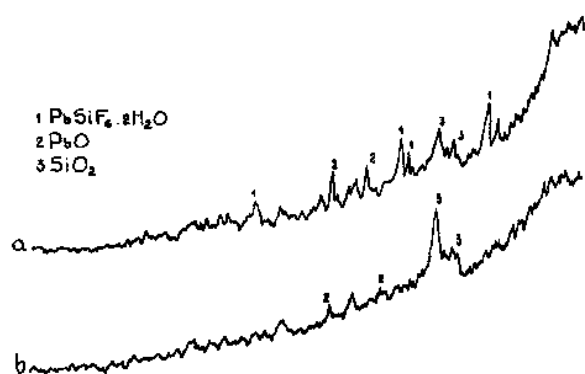


Fig. 1. X—ray structural analysis of sediments obtained after treatment of samples of toothpaste “Puro—Dent” - Curve A: according to BSS 15784—83 - Curve B: according to the methodology offered; a – by Bulgarian State Standard b – by new-established method

sired effect. This is the reason why the twofold preliminary treatment of the analyzed sample with 4 cm³ conc. HNO₃ was combined with a three-hour fusion not at 450 °C, but at 800 °C — the highest allowable temperature with respect to the volatility of some of the determined elements. The results are presented in Table 6.

From the data it is seen that Cu, Cr, and Ni pass thoroughly in the filtrate. The degree of extraction of Pb (98.7%) is also acceptable, as is relatively the one of Mn (92.2%). Only Zn remains captured by the separated sediment. An attempt to explain the obtained results was made, by X-ray analysis of the sediments, isolated after the treatment of the sample of the toothpaste “Puro Dent” (Figure 1). In the first sediment, obtained in accordance with [1], in addition to a phase of SiO₂, significant amounts of PbSiF₆·2H₂O and PbO were found. This fact explains the results of the determination of Pb, shown in Table 3, according to which the predominant part of it is discovered in the isolated sediment. It is evident that the 450 °C fusion can not lead to complete thermal decomposition of PbSiF₆·2H₂O. At the same time in the sediment, obtained after the preliminary treatment of the sample with conc. HNO₃ and fusion at 800 °C there are only traces of PbO, and the pique corresponding to PbSiF₆·2H₂O is altogether reduced (Figure 1 curve b).

It becomes clear that the treatment at the higher temperature of 800 °C enhances the thermal decompo-

sition of PbSiF₆·2H₂O, as well as the complete destruction of the organic compounds, contained in the analyzed samples. A similar effect is achieved by the preliminary treatment with conc. HNO₃.

CONCLUSIONS

As a result of the investigation carried out, it became clear that for the correct determination of some heavy metals, including the most commonly analyzed amounts of Pb and Cu, the methodology for preliminary chemical preparation of the samples of toothpastes regulated by BSS—15784—83 is unacceptable. Evidently, it due to the highly complicated composition of toothpastes, its application does not lead to effective extraction of the heavy metals. Hence the following method for preliminary chemical preparation of samples of toothpaste is proposed: 10g (0.0002 g) of toothpaste, measured in a porcelain crucible with 70 cm³ are heated cautiously on a sand bath, until the evaporation of fumes ceases. After that 2 cm³ conc. HNO₃ are added and the sample is heated again on a sand bath until the absence of nitrogen oxides is detected. The procedure is carried out four times (total quantity of the HNO₃ used — 8 cm³). After that the crucible is put in +0 cold temperature-regulated furnace, and the temperature is increased at a speed of 100 °C/hour up to 800 °C. The residue after the fusion is dissolved in 10 cm³ HNO₃ (1 : 1), let to fume carefully on a sand bath to dry condition and the procedure is repeated. The residue obtained is dissolved in hot distilled water acidified by the addition of several drops of HNO₃, and is filtered through a filter with miniscule particles in a measurement flask of 50 cm³ volume. After cooling down, distilled water is filled up to the mark of the flask.

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