

Determination of silver in cosmetic products by microwave plasma - atomic emission spectrometry

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The potential of a new spectral method, namely, microwave plasma atomic emission spectrometry (MP-AES), for determination of silver in various types of cosmetic products was studied. Instrumental operating parameters as nebulizer flow rate of nitrogen ($L \text{ min}^{-1}$) and viewing position are optimized.

Three types of cosmetic products are tested, i.e. face cream, body lotion and tooth paste. All samples were digested with HNO_3 and H_2O_2 by hot plate heating ($\text{DF}=50$) and then face cream and body lotion were diluted prior analysis by an additional factor of 40. Tooth paste was analyzed directly after digestion because of the lower content of Ag in the sample.

The four available wavelengths of silver in the MP-AES library (328.068, 338.289, 520.907 and 546.549 nm) were explored and the following instrumental limits of detection were obtained: 1.9, 2.3, 81, 98 $\mu\text{g L}^{-1}$, respectively. The study of spectral interferences in presence of sample matrix shows that only in the toothpaste there is a risk of interference due to neighbor titanium lines on 338.377 and 521.038 nm.

It was shown that all sample matrices did not cause a significant non-spectral effect on emission signals of Ag (<5%), at the specified above dissolution procedure and the proposed dilution factors. All measurements were done by external calibration with aqueous standard solutions.

The recovery of spikes of analyte to real samples is in the range 95-105%. The accuracy of the measurement is verified by independent ICP-MS determination. Obtained limit of quantification for the most sensitive emission line 328.068 nm is 0.32 mg kg^{-1} , which allows successful application of microwave plasma atomic emission spectrometry for determination of silver content in different cosmetics. The developed method is a fast, accurate and cheaper alternative to ICP-MS for controlling the silver levels in a variety of personal care products.

Keywords: MP-AES, ICP-MS, silver, cosmetics, analysis.

INTRODUCTION

Silver is a common addition in a variety of cosmetic products due to its well known antibacterial, antimicrobial and antifungal properties [1, 2]. Since silver is one of the most expensive metals, the cosmetic manufacturers often speculate on the exact content of Ag in their products. The most frequently used methods for quantification and control of the metal content in personal care products manufacture are fast, multi-element and generally very expensive [3, 4].

Microwave induced plasmas as alternative sources for atomic emission spectrometry have been rarely used in the last decade for determination of silver [5, 6] because of the lower detection power in comparison to ICP-OES [7].

Microwave induced nitrogen-based plasma working at atmospheric pressure was successfully interfaced to an atomic emission spectrophotometer (MP-AES) resulting in a next generation of spectral instrumentation for simultaneous determination of major and minor elements in a variety of environmental and industrial objects.

As MP-AES combines the multi-elemental

capabilities of an emission source with eliminating the need of expensive gases to support plasma, it is often defined as a cheaper alternative to FAAS and ICP-OES. Since 2012, when the instrument was first released by Agilent, the method has received a variety of practical applications. Ozbek and co-authors developed methods for determination of different elements in wines [8], cheese [9], bread [10] and rice samples [11]. MP-AES was also applied for analysis of waters [12], soils [13], plants [14], leather [15] and compost [16]. Besides the typically explored trace and alkaline elements, the method was also used for determination of rare-earth elements in waters, plants [17] and ores [18]. A few articles cope with the use of hydride generation MP-AES for determination of As and Se [19–22]. The vast variety of explored matrices and elements shows the potential of MP-AES to become a cheaper multi-element alternative to FAAS in the analytical laboratory. Furthermore, the method is often compared to ICP-OES [16, 17] and even ICP-MS [14].

The aim of the present study is to show the applicability of MP-AES for fast, cheap and

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EXPERIMENTAL

MP-AES 4200, Agilent and ICP-MS 7700, Agilent are used for all measurements after external calibration. ICP-MS determination is done under standard measurement conditions on isotopes ^{107}Ag and ^{109}Ag . ^{103}Rh is used for internal standard.

Samples are prepared as follows: approximately 0.5 g of the samples (face cream, body lotion and tooth paste) were treated on a hot plate with 10 mL of concentrated nitric acid (Fluka™) and 2 mL of 30 % H_2O_2 (Valerus Ltd). After digestion the solutions were left to cool down and diluted to 25 mL with doubly distilled water (BDW). Blank samples were prepared as well. Tooth paste was measured directly by MP-AES and with additional dilution factor 20 for ICP-MS. Face cream and body lotion were measured respectively with additional DF=40 for MP-AES and DF=100 for ICP-MS. Silver standard 1000 mg L^{-1} is purchased from Merck. An aliquot of IS Rh (CPA-spectr™) was added to the samples and standards prior to ICP-MS determination. All of the used stock standards are traceable to NIST. Calibration and working solutions are prepared with BDW and acidified with 0.5% p.a. nitric acid where necessary.

RESULTS AND DISCUSSION

Instrumental optimization

The Agilent MP-AES 4200 instrument allows the operator to optimize working parameters as nebulizer flow rate and plasma view position in such manner as to achieve the best sensitivity for a particular case. Optimization of both parameters was done in order to establish the best conditions for silver analysis using all wavelengths available in the spectral library of the instrument (Table 1).

Nebulizer flow rate affects both the size of aerosol droplets, the amount of analyte entering the plasma and the time that the analyte spends in the source. For this reason, nebulizer flow rate is an essential parameter that influences sensitivity. Optimization of N_2 flow rate was done for all wavelengths in the interval $0.3 - 1 \text{ L min}^{-1}$. Results for two of the studied Ag lines are presented on Figures 1 A and B for 328.068 and 546.549 nm.

View position was also optimized using the software option. The results for all tested lines were

very similar with optimum at the zero point – standard view position which is located coaxially to the central axis of the plasma discharge (Fig. 2).

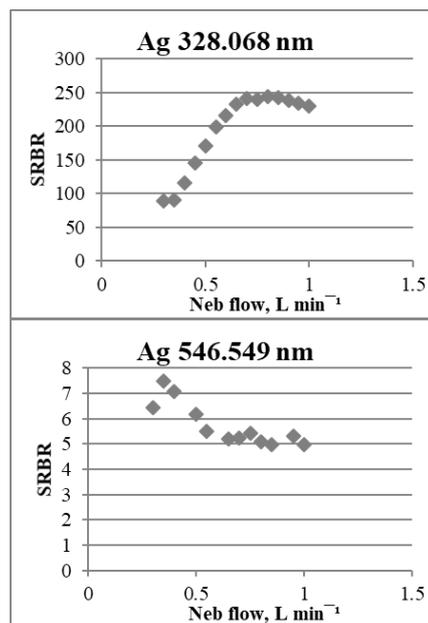


Figure 1. Influence of nebulizer flow rate on the corresponding signal-ratio-to- background-ratio (SRBR) for two Ag lines – 328.068 nm and 546.549 nm.

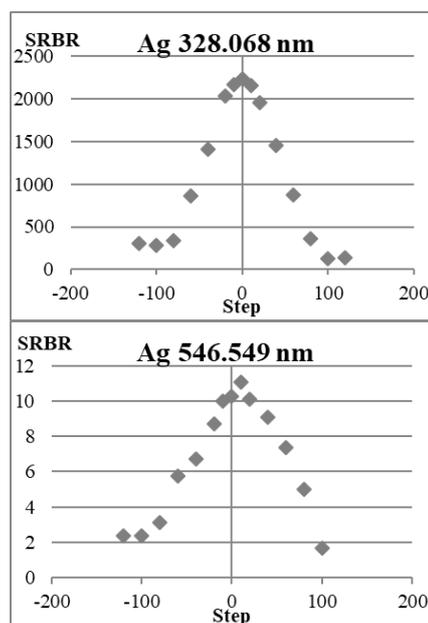
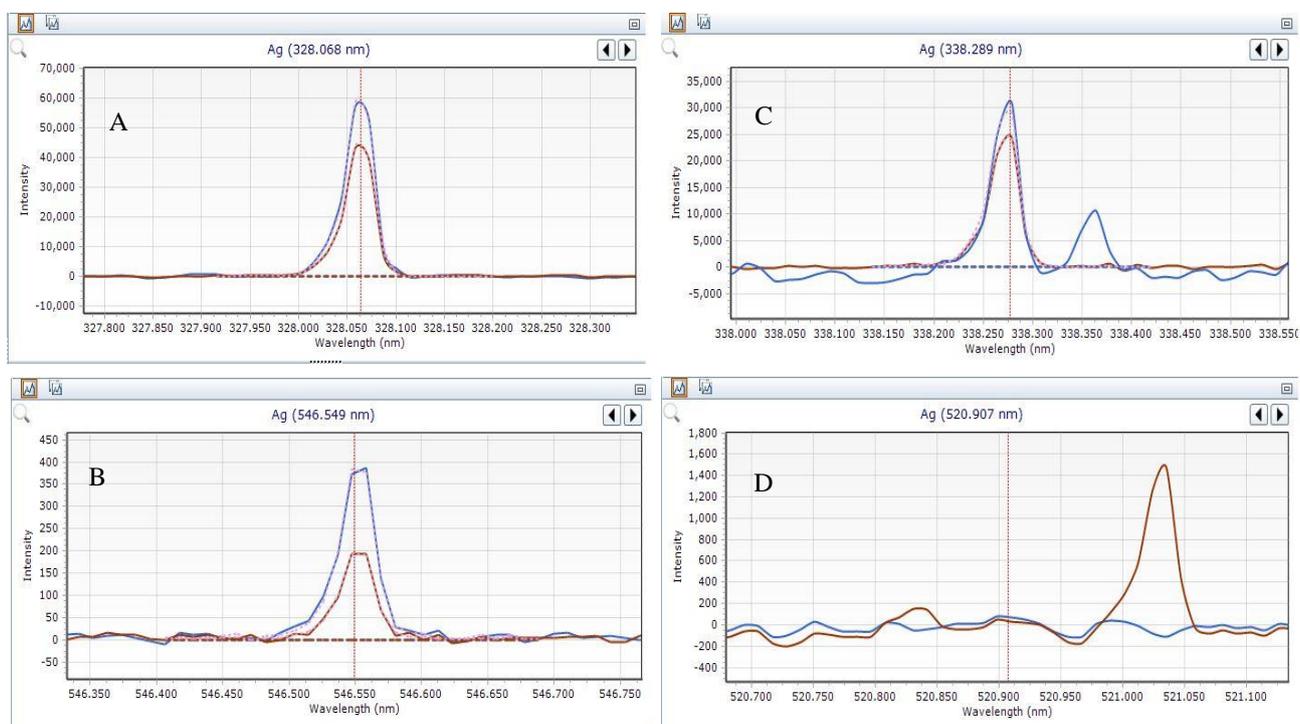


Figure 2. Influence of view position on the corresponding signal-ratio-to- background-ratio (SRBR) for two Ag lines – 328.068 nm and 546.549 nm.

Table 1. Emission lines of silver, type of emitting particle, relative intensity, order in spectral library and close lines of titanium.

Ag				Ti			
Wave-length, nm	Type of line	Relative Intensity	Transition energy (eV)	Wave-length, nm	Type of line	Relative Intensity	Transition energy (eV)
328.068	I	461836	3.78				
338.289	I	257077	3.66	338.377	II	76893	3.66
546.549	I	2361	6.04				
520.907	I	1440	6.04	521.038	I	13189	2.43

**Figure 3.** A-D Spectral profiles of Ag emission lines obtained for acidified water solution of Ag^+ 0.5 mg L^{-1} (red line) and toothpaste sample solution.

The influence of nebulizer gas flow rate on the sensitivity is much more pronounced than the viewing position. Optimum of 0.8 L min^{-1} is obtained for lines 328 and 338 and $0.3\text{-}0.35 \text{ L min}^{-1}$ for lines 546 and 520 nm. The behavior of the emission signals is consistent with what is expected in terms of their excitation energy. As the first couple (328 and 338 nm) belongs to the “soft” atomic lines (see Table 1) with low transition energy, increasing the nebulizer flow rate will stimulate production of finer aerosol droplets and corresponding enhancement of transport efficiency. Therefore, for these lines higher nitrogen flow rates are preferable. The second couple of lines (520 and 546 nm) are “hard” lines and for them lower nebulizer flow rate will ensure longer residence time in the hot plasma region needed for effective excitation.

Spectral interferences

A review of the MP-AES library showed that there are only four wavelengths for measuring silver. All of the lines are atomic with significant

differences in relative intensities (Table 1). The available lines were studied for potential spectral interferences from matrix components in the studied cosmetic products. There are strict requirements for cosmetic products that are commercially available. They concern both their purity (i.e. ensuring low levels of metal concentrations in them) and the declaration of all the main ingredients. After comparing information on the composition of the tested samples with the spectral library of the MP-AES instrument, we assumed that the only potential risk of spectral interference in silver analysis could be caused by the presence of titanium. As this element is a major component in a variety of products, its presence should be taken into consideration during development of the analytical method.

Library data showed that two of the Ag lines could be possibly overlapped by highly intensive neighbor lines of Ti.

For evaluation of spectral interferences on the lines of Ag two solutions were compared – acidified standard of silver and dissolved sample

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with appropriate dilution factor. No spectral interferences were observed for face cream and body lotion – measured concentration of silver on all wavelengths in these samples is practically identical. In contrast, tooth paste showed different behavior most probably because of the high content of TiO₂ in the sample. On Figures 3 A-D are presented signals obtained by measuring samples (tooth paste – blue line) and acidified water

solution of silver 0.5 mg L⁻¹ (red line). Results show that sample matrix does not lead to spectral interferences for lines 328 and 546 nm. In the case of the other two wavelengths it could be seen that neighbor emission lines of Ti emerge. Besides this it could be noted that the sample matrix changes the background which could lead to serious mistakes in calculating analyte concentration.

Table 2. Measured concentration of silver in tooth paste sample on different lines (n=3).

	328.068 nm	338.289 nm	520.907 nm	546.549 nm
Conc., mg L ⁻¹	0.15 ± 0.003	0.19 ± 0.003 0.15 ± 0.02*	< LOD	0.15 ± 0.018

* The given result is obtained after mathematical correction of Ti spectral interference.

Table 3. Threshold concentration of Ti in solution, mg L⁻¹

Ag	328.068 nm	338.289 nm	520.907 nm	546.549 nm
C _{threshold} , mg L ⁻¹	No	0.22	0.46	No

Table 4. Recovery of standard additions of Ag to samples (n=3)

Spike concentration	328.068 nm		338.289 nm		Spike concentration	328.068 nm
	R, %		R%			
	Face cream	Body lotion	Face cream	Body lotion		
0.50 mg L ⁻¹	106±7	102±3	106±7	101±3	0.05 mg L ⁻¹	104±5
1.0 mg L ⁻¹	102±4	103±5	101±4	102±4	0.10 mg L ⁻¹	101±4
2.0 mg L ⁻¹	100±5	100±4	101±3	101±5	0.20 mg L ⁻¹	103±6
	DF=2000					DF=50

Measured concentration of silver in the sample on different lines is presented on Table 2. The result obtained at a measurement of 338 nm is by about 40% lower compared to the free spectral lines of Ag, which can be caused by an improper background correction due to the nearby titanium line. The severe matrix interference in combination with the low sensitivity of the line at 520 nm resulted in a negative signal value for toothpaste solution after automatic background correction. For the interfered spectral lines of Ag, automatic background correction is inappropriate, hence only a left side correction at 338.15 nm and 520.694 is recommended. This leads to 25% higher concentration of Ag measured on 338 nm. Even in this case the contribution of Ti as interfering element should be additionally estimated.

It could be concluded that all emission lines are appropriate for determination of silver in the tested face cream and body lotion. Ag in samples with high content of Ti could be measured on line 328 nm or if the concentration of the analyte is higher, the less sensitive line (546 nm) could be also used.

Threshold concentration of Ti was determined to specify the limitation of measuring silver in the presence of the interference. Threshold levels are calculated as Ti concentration that gives a

statistically distinct signal at the respective analyte wavelength (i.e., the interfering signal is equal to 3×standard deviation of background). Results are presented in Table 3. The measured concentration of Ti in the sample with DF=50 is 0.35 mg L⁻¹. This means that for the spectral line of 338.289 nm there is a real strong interference effect that requires additional correction. The interference factor of Ti on this line was estimated as 1800 and after mathematical correction the estimated concentration of in tooth paste on this Ag line (338 nm) is statistically identical to the ones for free spectral lines (see table 2). It should be noted that additional correction of Ti interference on 338 nm reflects in increased uncertainty. Concerning the latter line at 520 nm the presence of Ti is below the threshold concentration, but the weak sensitivity makes this line impractical when measuring real samples with a low silver content.

Non-spectral matrix effect

The three tested samples were examined for non-spectral matrix effect with appropriate dilution factor. The concentration of Ag in the samples could be measured with dilution factor 2000 for face cream and body lotion and 50 for tooth paste. As cosmetic products consist of a comparatively

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 “light” matrix, severe non-spectral effects were not expected. In order to investigate if there is some matrix influence on emission signals, real samples were spiked with known amount of silver. Concentration of spikes is selected accordingly to the concentration of silver in the real samples. The recoveries of three spikes to each of the studied

cosmetic samples are presented on Table 4. For face and body lotion results are identical for all wavelengths. Quantitative recovery shows that the matrix does not lead to suppression or enhancement of the analyte signal in real samples, hence a simple external calibration by water standards of Ag is adequate strategy.

Table 5. Comparison of MP-AES and ICP-MS results for Ag in cosmetic products.

	MP-AES (n=3)	ICP-MS (n=5)
	conc., %	conc., %
Face cream	0.35±0.005	0.34±0.014
Body lotion	0.45±0.006	0.45±0.009
	conc., mg kg ⁻¹	conc., mg kg ⁻¹
Tooth paste	7.76±0.2	7.80±0.12

Table 6. MP-AES limits of quantification (10×stand. deviation) for Ag (DF=50).

Ag, wavelength	328.068 nm	338.289 nm	520.907 nm	546.549 nm
MLOQ, mg kg ⁻¹	0.32	0.38	13.4	16.2

The concentration of silver in tooth paste and corresponding standard additions are above LODs only for 2 lines, 328 and 338 nm, but for the second one an additional correction of spectral interference is needed. Therefore, the free line is recommended for real samples analysis as less problematic. The recoveries of the standard additions measured on this line are in the interval 101-104 %. Results show that DF=50 allows measuring Ag without a risk of non-spectral matrix effect. Further attempts to decrease the dilution factor to 25 lead to significant change in the background even for line 328 nm and made the analysis impossible.

Analytical characteristics of the MP-AES method

Due to the lack of an appropriate certified reference material for the determination of silver in cosmetic products, the accuracy of the proposed MP-AES method was demonstrated by comparison with an alternative ICP-MS analysis (Table 5). Ag content in the three samples is measured by mass spectrometry with appropriate dilution factors (see Experimental).

Concentrations of the analyte obtained by both methods are statistically identical which demonstrates the applicability of MP-AES for determination of silver in a variety of cosmetic products.

The intra-laboratory reproducibility was assessed by repeating the analytical procedure described above for determination of Ag in all studied objects in three different days. The obtained relative standard deviations (RSD, %) were as follows: 1.96, 2.8 and 3.7 for face cream, body

lotion and tooth paste, respectively. The target reproducibility of the method was calculated according to the Horwitz model [23], taking into account the correction factor of 2/3 for intra-laboratory comparison. As the silver content of the tested products significantly differs, the target reproducibility for *face cream* and *body lotion* was estimated as 3.1% RSD, while for trace levels of Ag in the *tooth paste* the corresponding target RSD was 7.7%. As it can be seen from the above results, the internal laboratory reproducibility of the method is better than that predicted by the Horwitz model.

Method detection limits are presented on Table 6. Obtained results show that the method is sufficiently sensitive for quantification of Ag in different cosmetic products.

CONCLUSIONS

The performed investigations proved that the new instrumental technique MP-AES is an adequate alternative to ICP-MS for determination of silver in a variety of cosmetic products. The analytical performance is easy, cheap and fast, allows quantifying Ag content by simple external calibration with limits of determination between 0.3-16 mg kg⁻¹. Two emission lines at 328.068 and 546.549 nm are recommended, since they are free from spectral interferences, while for the next two lines 338.289 and 520.907 nm the presence of Ti in toothpastes or sunscreen creams should be taken into consideration because of the risk of spectral interferences originated by neighbor emission lines. The estimated threshold concentrations of

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interfering element give fast and reliable information about the need of additional mathematic correction of real interference effects.

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