

Spectrochemical determination of lead in wines*

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The determination of lead in wines of different origin was performed by means of atomic emission spectroscopy with argon stabilized DC. U-shaped arc and electrothermal atomic absorption spectrometry. The comparison of the results obtained by the direct and standard addition method has indicated the presence of a depressive effect of the complex organic matrix. The effect is avoided successfully by mineralization, as well as by dissolution of the samples. Thus, a relative simple but precise and sensitive method involving the application of a stabilized arc and photoelectric detection with time integration of the emission signals is recommended for the determination of low concentrations of lead in wines. The complex organic matrix was investigated by recording the IR spectra of different wine fractions.

Keywords: lead, U-shaped arc, GFAAS, organic matrix.

INTRODUCTION

A large number of elements occur in foodstuffs as environmental contaminants, sometimes at levels which are considered to be toxic.^{1,2} The toxic effect of lead at low levels in the environmental is a cause of increasing concern and growing interest in the determination of its concentration in foodstuffs.

The trend in dietary behavior in the last few years has seen an increased consumption of fruit and beverages such as wine, beer, soft drinks and juices. Although the amount of lead in these samples is very low, the daily dietary intake may be physiologically significant.³ Therefore, the determination of lead in such samples requires the use of techniques which provide high sensitivity and very low detection limits.

The spectrochemical methods recommended for direct determination of the mineral components in wine are inductively coupled plasma atomic emission

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spectrometry (ICP-AES),⁴ electrothermal atomic absorption spectrometry (ETAAS)⁵⁻⁷ and hydride generation atomic absorption spectrometry (HGAAS).^{8,9} Potentiometric stripping analysis¹⁰ and anode stripping voltammetry¹¹ are electrochemical methods also suggested for the direct determination of trace elements in wine. Different conclusions have been reached about the possible influence of the matrix on trace element determination in wine samples. Therefore, in this work, two spectrochemical methods for the determination of the lead content in wines were applied: argon stabilized DC U-shaped arc with aerosol supply AES and ETAAS. The concentrations of Pb in five various red and white wines from different Serbian wine-growing regions were determined. The direct determination of Pb, with standards containing ethanol, was used in all methods. In order to investigate the possibility of a matrix effect when analyzing these relatively complex natural samples, the method of standard addition, as well as mineralization of the samples by an H₂O₂+HNO₃ mixture were applied.

EXPERIMENTAL

Instrumentation I

In the first part of the experiment, a U-shaped low current arc stabilized with an argon vortex was applied as the excitation source in atomic emission spectroscopy (AES). The experimental set-up and main characteristics of this arc are described elsewhere.¹² The operating conditions and equipment used in the AES with arc excitation are presented in Table I. The spectrograph was adapted to a one-channel monochromator. The needed detectability for the determination of lead in wines by AES was achieved by photoelectric registration and computer program that enabled the integration of the emission signals in the chosen optimal times. Such a method lowered the detection limit by about one order of magnitude.¹³ The optimal integration time for the determination of lead under the applied experimental conditions was 30 s. The analytical line used was Pb I 405.78 nm. The solutions were nebulized into the plasma by application of a Meinhard concentric glass nebulizer, type C, connected with a double-pass spray chamber.

Instrumentation II

A Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer with a graphite furnace HGA 400, with pyrolytic graphite tubes was used. A spectral bandwidth of 0.7 nm was selected to isolate the Pb I 283.3 nm line.

The temperature and gas flow rates were optimized for these determinations and are presented in Table II. An aliquot volume of 20 µl of the standard and sample solutions was introduced into the graphite furnace.

Instrumentation III

The IR spectra of different wine fractions were recorded in the range 4000-250 cm⁻¹ with a Perkin-Elmer 983 G spectrophotometer using the KBr pellet technique.

The separation of the wine samples into different fractions, which were analyzed by IR spectroscopy, was performed according to the scheme given in Table III.

Solutions and reagents

Ethanol (redistilled before use), HCl (analytical grade) and deionized water were used for the preparation of the solutions. To prepare the standard solutions, the required volumes of ethanol and stock solutions of lead (1000 mg/l) were added to a volumetric flask and made up to the final volume with a) 3 % (v/v) HCl or b) Milli-Q water. The calibration standard matrix must be matched to the

samples using ethanol. So, standard solutions containing the same quantity of ethanol as the wine sample, *i.e.*, $\approx 10\%$ (v/v), were prepared. The concentration range of lead in the standards was from 0.1 to 0.5 $\mu\text{g/ml}$. All the determinations were performed from the line peak heights. For AES, standard solutions of lead with ethanol, (10 %, v/v), 0.5 % KCl, as spectrochemical buffer, and HCl, in the same way as the standard solutions. The standards for the direct determination of lead in wine were in the concentration range from 0.01 to 1.00 $\mu\text{g/ml}$ due to the wider dynamic range of the applied arc-AES method than the ETAAS method.

Procedure

In the case of the direct determination of lead by ETAAS, the wine samples were analysed without any pre-treatment. If a method requires mineralization of solid samples it increases both the analysis time and the risk of sample contamination.

Measurements were performed with and without a matrix modifier. As recommended in the literature,¹⁴ modifier solutions of ammonii dihydrogenphosphas were used in order to obtain better reproductibility and detectability of lead by ETAAS.

In order to investigate possible matrix effect, the standard addition method was performed with three standards. The required concentration of the standard solutions was defined on the basis of the results of the direct determination. The final volume of the standards and the wine samples was equal, after standard addition.

Mineralization of the wine samples was applied for the same purpose as the standard addition method. The procedure was performed as follows: 100 ml of wine sample was evaporated in an open vessel to a volume of 20 ml and 10 ml of concentrated HNO_3 (p.a. Merck) and 20 ml of concentrated H_2O_2 (Merck) were added. The solution was again evaporated almost to dryness, transferred to a volumetric flask of 50 ml and diluted with bidistilled water.

The wine samples were also diluted with bidistilled water in different ratios to minimize the possible matrix effect.

RESULTS AND DISCUSSION

All the obtained results are presented in Table IV.

It can be concluded that results of direct lead determination by AES are about 50 % lower than those obtained by the standard addition method. This is obviously evidence of a strong depressive effect from the complex matrix of wine. In order to decrease the organic matrix effect, two procedures were applied. In one case the wine samples were diluted with different volumes of water. A 1:1 quantitative dilution of the samples resulted in a satisfactory minimization of the matrix effect, as presented in Table IV. The matrix effect was also removed by mineralization of the samples. The obtained results for these two methods are generally in good agreement with those of the standard addition method. A partial agreement between the results of the standard addition method by arc-AES and ETAAS was also attained. The better agreement should be obtained if a more appropriate modifier in the case of ETAAS was applied.

The strong depressive effect of the complex organic matrix was investigated by application of IR spectroscopy to dry residues of the wine samples.¹⁵ The IR spectra of wine fractions obtained according to the scheme given in Table III are presented in Figs. 1 and 2, as examples. The IR spectra of fraction II (extracted by

alcohol and insoluble in water), presented in Fig. 1, for all the investigated wines show the presence of a complex mixture of organic compounds, qualitatively almost the same for all samples. A slight difference was noticed in the case of fraction III (extracted by ethanol and soluble in water). The IR spectra of the fraction III of one red wine are given in Fig. 2. These spectra also show the presence of a complex organic matrix. It is obvious that the matrix effect is always present but its magnitude depend on the type of wine.

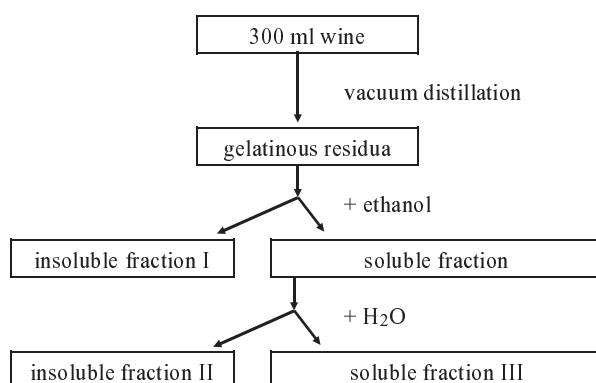
TABLE I. Experimental and operating conditions for EAS

Spectrograph	PGS-II
Grating	Baush & Lomb 600 grooves/mm
Photomultiplier	Hamamatsu R-106
Enter and exit slit	200 μm
Slit height	1 mm
Nebulizer	Meinhard type-C
Arc current	7.5 A
Total flow rate of Ar	3 L/min

TABLE II. Temperature program for lead determination by direct injection of wine into the graphite tube

Step	Temperature/ $^{\circ}\text{C}$	t_{ramp} (s)	t_{hold} (s)	Flow rate ml/min Ar
Ashing	110	10	30	300
Mineralization	500	5	30	300
Atomisation	2100	0	7	0
Cleaning	2900	2	2	300

TABLE III. Separation of wines into various fractions



On the basis of the presented results it can be concluded that each of the applied techniques, AES and ETAAS, has its advantages and disadvantages and which one

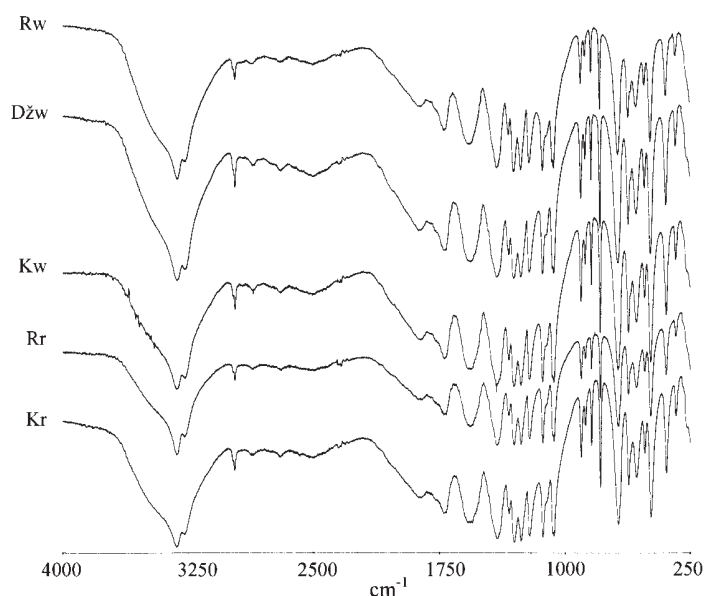


Fig. 1. IR spectra of fraction II.

will be chosen depends on the sample quantity, the concentration range of the analyte and the required precision of the determination. It is obvious that the simplest and the most rapid method for lead determination in wines involves dilution of the wine samples and their direct nebulization into an argon stabilized U-shaped arc. This excitation source and method of signal detection enable the determination of analyte over a wide concentration range with high precision and with a very low detection limit.

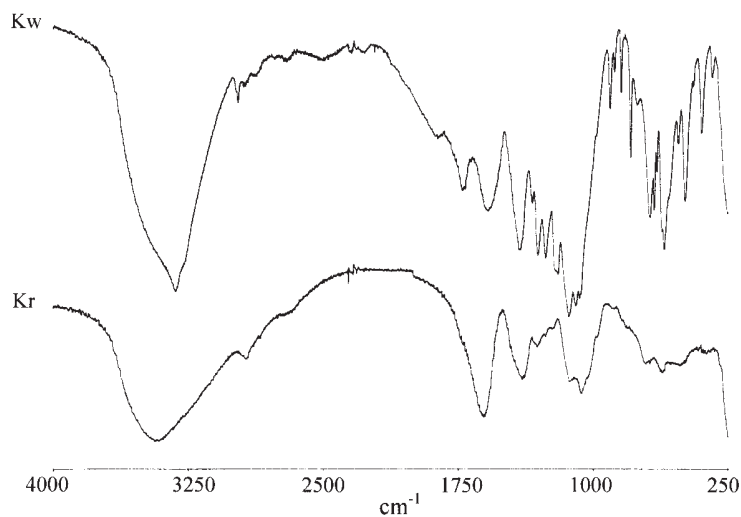


Fig. 2. IR spectra of fraction III.

TABLE IV. Results of lead determination in wines, ng/ml

Sample	Direct method AES	Standard addition method AES	Dilution method AES	Mineralization HNO ₃ /H ₂ O ₂ AES	Standard addition method ETAAS
Rw	56	108	120	116	145
Džw	44	110	110	131	104
Kw	78	117	120	128	105
Rr	106	220	170	143	224
Kr	83	145	140	141	173

Rw and Rr - Rubin white and red, Kw i Kr - Kosovo white and red, Džw - Džervin white

CONCLUSION

Two spectrochemical methods for determination of Pb in wines are applied and their results compared: AES and ETAAS. The aim was to find the best and the simplest way for such an analysis. Wine as a natural material has a very complex matrix the influence of which cannot be neglected. Direct nebulization of wine samples into an argon stabilized U-shaped arc and photoelectric registration of the integrated emission signals have indicated a strong depressive matrix effect. In order to avoid this effect, mineralization, as well as dilution of the wine samples was applied. The results obtained by these methods are in satisfactory agreement with the results obtained by the standard addition method. Better agreement between the results obtained by the standard addition method and ETAAS and/or AES could be expected if a more convenient modifier is applied.

ИЗВОД

СПЕКТРОХЕМИЈСКО ОДРЕЂИВАЊЕ ОЛОВА У ВИНИМА

МИРЈАНА ТРИПКОВИЋ,^a МАРИЈА ТОДОРОВИЋ,^b ИВАНКА ХОЛЦЛАЈТНЕР-АНТУНОВИЋ,^c
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Одређивање олова у винима различитог порекла вршено је применом атомске емисионе спектроскопије са аргоном стабилисаним луком U-облика и атомске апсорпционе спектроскопије са графитном киветом. Поређење резултата добијених директном и методом стандардног додатка показало је да постоји знатан депресивни ефекат сложене органске основе. Ефекат је успешно избегнут минерализацијом или разблажењем узорка. Комбинацијом разблажења узорка и применом стабилизованог лука и фотоелектричне детекције са временском интеграцијом емисионих сигнала развијена је једноставна и прецизна метода за одређивање ниских концентрација олова у винима. Комплексан органски матрикс испитиван је снимањем ИС спектра различитих фракција вина.

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