

DATA ANALYSIS OF VARIANCE IN ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF HAZARDOUS MICROELEMENTS Ni, Pb, Cd FROM POLYETHER POLYOLS

Ion Gh. TĂNASE,^a Alexandru PANĂ^{b*} and Mihaela PANĂ^c

^a University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Regina Elisabeta 4-12, 030018, Bucharest, Sector 1, Roumania

^b SC Oltchim SA, Uzinei 1, Rm. Vâlcea, 240050, Roumania

^c National Agency of Romanian Waters, Quality of Water Laboratory, Remus Bellu 6, Rm. Vâlcea, 240204, Roumania

Received December 12, 2007

The process for obtaining polyether polyols takes place discontinuously, in batches. Therefore, when the lots are prepared it is necessary to have a good homogenization of the batches. Starting from these considerations a study of the analysis of variance can give information regarding the number of samples necessary to obtain a good characterization of the product from the point of view of the content of hazardous metals such as Ni, Pb, Cd and can also give quantitative information regarding the part of the total variance which can be attributed to the method of sampling and the part corresponding to the method of analysis. Similarly, on basis of the analysis of variance at the limits (low and high) of linear range it is possible to decide whether the linear function is suitable for the calibration of an atomic absorption spectrometer.

INTRODUCTION

Determination of metals in various organic matrices is conveniently achieved by means of atomic absorption spectrometry (AAS) measurements.¹ The determination of trace metals in lubricating oils using atomic spectrometric methods has been recently reviewed.² The importance of such analyses for technical diagnostics as well as the specific sample characteristics related to the analyte form (metallo-organic and metal particles) was discussed. Problems related to sample pre-treatment for appropriate sample introduction and calibration have been addressed as well as the strategies to overcome them. Matrix elimination method using different hydrogels for the determination of precious metals in ores using electrothermal AAS was reported in order to improve the precision and accuracy of the analytical results.³ Gasoline, diesel, ethanol and recently biodiesel are the four types of fuel used for automobile, truck and other transportation vehicle. The analytical methods that have been developed for metal and metalloid

quantification in automotive fuel have been reviewed.⁴ The main atomic spectrometric techniques used for trace metal and metalloid determination in fuels, particularly atomic absorption spectrometry with flames, graphite furnaces and with chemical vapor generation, and inductively coupled plasma coupled with optical emission and mass spectrometry are presented, including the different sample preparation procedures proposed for these techniques.

Data literature focused on determinations of different metallic ions in polyether polyols matrix is lacking. It is the aim of this paper to propose a method based on AAS technique for determination of three hazardous microelements (Ni, Pb and Cd) in this complex matrix and to discuss the analytical outcome from statistical point of view.

THEORETICAL BACKGROUND

The variance of a set of AAS measurements is a value obtained on basis of statistical processing of analytical data. In statistics, the analysis of

* Corresponding author: panaalex@oltchim.ro

variance is a collection of statistical models and their associated procedures, in which the observed variance is partitioned into components due to different explanatory variables. The variance s^2 of a set of n measured value x_i equals the arithmetic mean of the quadratic deviation of the measurements with respect to their average value \bar{x} :⁶

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \quad (1)$$

Generally, the analysis of variance is used in laboratory according with the standard methods only to decide whether a linear calibration function is fitted. The originality of this work consists in that we try to extent this analysis of variance to the other tasks. Therefore, the analysis of variance is very important for the subdivision of the total variance of a set of observations into partial variances that are attributed to well defined sources (method of sampling or analysis); for the determination the number of samples necessary to be analyzed in order to ensure a certain level of confidence, a certain uncertainty and a certain relative standard deviation; to confirm the fact that the scattering of values of two populations placed at the limits of a linear calibration curve are constant and that a linear calibration function is fitted.

The analytical data obtained from different samples of the same material are distributed around a mean value. To determinate the variances caused either by the method of sampling or by the method of analysis it can be assumed that from a given population of objects k samples are selected, each containing n_k objects. A better variance value of the parent population σ_0^2 is based on the

variance estimate within the sample and is called the within group variance s_w^2 :

$$s_w^2 = \frac{1}{k} \cdot \frac{1}{n_j - 1} \sum_{j=1}^k \sum_{i=1}^{n_j} (x_{i,j} - \bar{x}_j)^2 \quad (2)$$

The between groups variance s_b^2 is an estimate of the parent population variance σ_0^2 and is based on variance between the mean values of samples. The value s_b^2 can be calculated from the formula:

$$s_b^2 = \frac{n}{k-1} \sum_{j=1}^k (\bar{x}_j - \bar{x})^2 \quad (3)$$

The estimated value of σ_μ^2 (variance of mean value population μ) is equal to s_μ^2 and can be calculated from the following equation:

$$s_\mu^2 = \frac{(s_b^2 - s_w^2)}{n} \quad (4)$$

Generally, s_b^2 is bigger than s_w^2 , but if s_b^2 is smaller than s_w^2 then the difference between them should not be significant. If however the difference is significant, a mistake has been made in the calculation or during the measurement process. A non-zero contribution s_μ^2 to the variance between samples is interpreted as the introduction of an uncertainty within the analytical results due to sampling method. Sometimes s_w^2 is the uncertainty within the analytical results, caused by the method of analysis itself or by the distribution of x values in the parent population.

Determination of the ratio between the two variances s_b^2 and s_w^2 should be done on basis of an analysis variance scheme (given in Table 1).

Table 1

Scheme of Analysis of the variance

Source of variance	Sum of square	Number of degrees of freedom	Variances	Quantity estimated
Between samples	$S_b = n \sum_{j=1}^k (\bar{x}_j - \bar{x})^2$	$v_1 = k - 1$	$s_b^2 = \frac{S_b}{k - 1}$	$\sigma_0^2 + n \sigma_\mu^2$
Within samples	$S_w = \sum_{i=1}^n \sum_{j=1}^k (x_{i,j} - \bar{x}_j)^2$	$v_2 = k(n - 1)$	$s_w^2 = \frac{S_w}{k(n - 1)}$	σ_0^2
Total	$S_w = \sum_{i=1}^n \sum_{j=1}^k (x_{i,j} - \bar{x})^2$	$v_3 = nk - 1$		

Afterwards, using a statistical test F, the value $F_{\text{calc}} = \frac{S_b^2}{S_w^2}$ is calculated and compared with the critical values F_{crit} of the distribution F. If $F_{\text{calc}} > F_{\text{crit}}$ then s_b^2 is significantly bigger than s_w^2 .

Before making an analysis according to an indicated method it is necessary to determinate the necessary quantity of sample which does not affect the result of the analysis. In order to determinate the exact quantity of sample necessary for the analysis all the uncertainty sources that are included in the final result, *i.e.*, from sampling and from measurement, should be taken into consideration.

To establish, on mathematical basis, the number of samples to be collected it is necessary to take into account the weight of variances and the ratio between them. There are many situations of measurement as discussed below.

Measurement variance insignificant, sample variance significant

In this case it is necessary to calculate the number of samples to be collected. This can be done if some parameters, such as the standard deviation of measurement, the uncertainty of measurement and the level of confidence agreed, are known. Assuming a normal distribution of results, the limits of the sample mean \bar{x} are given by:

$$\bar{x} \pm \frac{t \cdot s_s}{\sqrt{n_s}} \quad (5)$$

where: \bar{x} - is the measurements mean, s_s - is the sample standard deviation, n_s - is the number of observations, t - is the value tabulated in the Student's distribution tables for $(n_s - 1)$ degrees of freedom at various confidence level percentages.

Equation (5) is written in the general case, considering uncertainty u , as:

$$\bar{x} \pm u \quad (6)$$

where: $u = \frac{ts_s}{\sqrt{n_s}}$ (7)

From equation (7) the number of samples to be collected can be calculated:

$$n_s = \frac{t^2 s_s^2}{u^2} \quad (8)$$

Measurement variance significant, sample variance insignificant

In this case it is necessary to use a representative sample and then to carry out n_A analyses:

$$n_A = \frac{t^2 s_m^2}{u_A^2} \quad (9)$$

where: u_A is the total uncertainty allowable in the analysis, s_m - the measurement standard deviation.

Measurement and sample variance significant

In this case a compromise between the necessary number of samples and the cost of sampling is accepted.^{7,8} Because both the sampling and the measurement affect the total uncertainty u_{total} , there is no unique answer:

$$u_{\text{total}} = t \left(\frac{s_s^2}{n_s} + \frac{s_m^2}{n_A n_s} \right)^{1/2} \quad (10)$$

In the calibration process of the equipment, for drawing the calibration curve a linear regression function or a polynomial one can be used. In the next step, according to Mandel, a statistical test F is applied in order to find out if the linear calibration model is not suited and a nonlinear model should be used.⁹

Usually, for the calibration of analytical equipment a linear regression function is desired. This procedure is based on measurement errors having their mean equal to zero and not to be correlated.¹⁰ That means that standard deviations should be constant in some points on the calibration curve. To establish if the standard deviations of two populations situated at the limits of the calibration function are equal a statistical test F should be used by testing the relationship between them working range.^{11,12} Two situations should be considered in order to take a decision regarding the homogeneity of variance over the linear range:

a. If $F_{\text{calc}} < F_{(f1; f2; 0,99)}$ the deviation between variances s_{min}^2 and s_{max}^2 is not significant;

b. If $F_{\text{calc}} > F_{(f1; f2; 0,99)}$ the deviation between variances s_{min}^2 and s_{max}^2 is significant.

The linear calibration function is considered to be suited for the linear range if the deviation between variances s_{min}^2 and s_{max}^2 is not significant.

EXPERIMENTAL

In order to carry out the study of analysis of variance a standard polyether polyol of type three-ol, commercially known as Petol 48-3MB, produced by Oltchim from glycerine, ethylenoxide and propylenoxide, mostly used industrially to obtain polyurethane foams, was used. In a store tank of 200 To capacity several batches of polyether polyol were randomly mixed and a number of 6 samples were successive collected over a short period time. Then, the concentration of Ni, Pb, Cd in these samples was measured. For each sample of polyol a number of 5 repeated analyses were made. Because the measurement procedure involves the calcination (4 hours at 380°C) of samples (5 g) and the transfer of the calcination residue into acid water solution HNO₃ 0.5%, the analysis of

these elements was carried out over a period of 4 weeks. During this period the samples were sealed and kept at controlled temperature between 15-30°C, to prevent their contamination or degradation.

To verify the homogeneity of variances, 10 repeated analyses were carried out, on each etalon solution of Ni, Pb, Cd, for the lowest and the highest concentration of the linear range.¹³⁻¹⁵ For the calibration of the instrument, stock solutions of metals (S) CertiPUR with concentration of 1000 mg/L, produced by Merck, were used. The following working calibration solutions were prepared for each species: 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ppb for Ni²⁺ and Pb²⁺; 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 ppb for Cd²⁺.¹⁶

The analytical instrument used was an Atomic Absorption Spectrometer, type SOLAAR 969, manufactured by UNICAM. Because the content of the metals of interest is at the ppm level, the measurements have been carried out by Electrothermal Atomization Technique using a Massman graphite furnace equipped with a graphite cuvette of ELC (Extended Lifetime Cuvettes) type (Table 2).^{17,18}

Table 2

Working parameters of AAS determinations

AAS parameters for Ni: wavelength – 232 nm; bandpass – 0.2 nm; lamp current – 80%					
Sample volume: 10 µL. Furnace parameters:					
The phase	Temp (°C)	Time (sec)	Ramp (°C/s)	Gas flow (ml)	The action
1	100	30	5°C/sec	0.2 L/min	-
2	250	10	5°C/sec	0.2 L/min	-
3	500	10	10°C/sec	0.2 L/min	-
4	1000	20	150°C/sec	0.2 L/min	-
5	2500	3	0°C/sec	Off	RD TC
6	2600	3	0°C/sec	0.2 L/min	TC
AAS parameters for Pb: wavelength – 217 nm; bandpass – 0.5 nm; lamp current – 90%					
Sample volume: 20 µL. Furnace parameters:					
The phase	Temp (°C)	Time (sec)	Ramp (°C/s)	Gas flow (ml)	The action
1	90	30	10°C/sec	0.2 L/min	-
2	250	20	10°C/sec	0.2 L/min	-
3	600	10	10°C/sec	0.2 L/min	-
4	700	10	150°C/sec	0.2 L/min	-
5	1200	3	0°C/sec	Off	RD TC
6	2500	3	0°C/sec	0.2 L/min	TC
AAS parameters for Cd: wavelength – 228.8 nm; bandpass – 0.5 nm; lamp current – 80%					
Sample volume: 5 µL. Furnace parameters:					
The phase	Temp (°C)	Time (sec)	Ramp (°C/s)	Gas flow (ml)	The action
1	100	30	5°C/sec	0.2 L/min	-
2	200	10	10°C/sec	0.2 L/min	-
3	300	20	150°C/sec	0.2 L/min	-
4	900	3	0°C/sec	Off	RD TC
5	2500	3	0°C/sec	0.2 L/min	TC

RESULTS AND DISCUSSION

The analytical data obtained from the measurement of the metals of interest, from 6 different samples, each being prepared and repeated 5 times, are showed in the Tables 3, 4, 5.

Based on analytical data obtained were calculated the variances (Table 6) between samples s_b^2 (caused by method of sampling) and the variances within samples s_w^2 (caused by the method of analysis).

Table 3

Analytical data obtained for Ni and used to the analysis of variance

Analysis No.	Sample No.	Analytical data of 5 analyses on 6 samples ($\mu\text{g/L}$)					
		1	2	3	4	5	6
1		120	124	120.5	122	122	122
2		121	123	120	122	119	119
3		120	123	119	121	119	121
4		120.5	122	120	121	120	120
5		121	122.5	119	119	121	122
Average value of sample, \bar{x}_j		120.5	122.9	119.7	121	120.2	120.8

Table 4

Analytical data obtained for Pb and used to the analysis of variance

Analysis No.	Sample No.	Analytical data of 5 analyses on 6 samples ($\mu\text{g/L}$)					
		1	2	3	4	5	6
1		15	15	15.5	15.8	15	14.9
2		15.1	14.5	16	15.7	15.1	15.3
3		15.4	14.9	16.3	15.5	15.3	14.6
4		15	14.8	14.5	15.9	15.2	15
5		14.9	15.3	14.9	16	15	14.9
Average value of sample, \bar{x}_j		15.08	14.9	15.44	15.78	15.12	14.94

Table 5

Analytical data obtained for Cd and used to the analysis of variance

Analysis No.	Sample No.	Analytical data of 5 analyses on 6 samples ($\mu\text{g/L}$)					
		1	2	3	4	5	6
1		10	11	10.3	10.1	10.9	10.1
2		10.4	10.6	10	10.2	11	10.4
3		10.15	10.5	10.15	10	10.5	10.1
4		10.05	10.55	10.3	10.15	10.1	10
5		10.1	10.8	10.4	10.1	10.2	10.6
Average value of sample, \bar{x}_j		10.14	10.69	10.23	10.11	10.54	10.24

Table 6

Results obtained in the analysis of variance

Sources of variance	Number of degree of freedom	Variance			Quantity estimated	
		Ni	Pb	Cd		
Between samples	$\nu_1 = 5$	s_b^2	6.095	0.572	0.276	$\sigma_0^2 + 5\sigma_\mu^2$
Within samples	$\nu_2 = 24$	s_w^2	1.025	0.133	0.054	σ_0^2

Comparing the results obtained, it is obvious that the variances between samples s_b^2 are bigger than the variances within samples s_w^2 . Using a statistical test F the values $F_{\text{calc}} = \frac{s_b^2}{s_w^2}$ were calculated and compared with critical values F_{crit} of the distribution F (Table 7). The critical value $F_{\text{crit}} = F_{(\nu_1, \nu_2, \alpha)} = F_{(5; 24; 0.05)} = 2.62$ was taken from the Fisher's table.²

From the analysis of the data shown in Table 7 it appears that the F_{calc} values, calculated for each analyte, are bigger than F_{crit} value, which demonstrates that the variance between samples s_b^2 is significantly bigger than the variance within samples s_w^2 . From the data obtained in the analysis of the variance it appears that we are in the situation when the variance of sampling is significant and the variance of method is insignificant. It is clear that for a correct evaluation

of the content of hazardous metals from the measured polyether polyols samples it is necessary to collect many more samples and to report as result the mean value of these measurements. In order to calculate the necessary number of samples to be analyzed n_s , according to equation (8), first it was necessary to calculate the relative standard deviations and extended uncertainties for a 95% level of confidence. Because in this study many variables (concentrations of Ni, Pb, Cd) of the same sample were evaluated, the value n_s should be estimated for each of these metals. The relative

standard deviations were obtained on basis of a repeatability study. To determinate the repeatability, nine similar standard solutions for each of the metals were prepared, situated in the middle of the working range: measurements of Ni (10 ppb), Pb (10 ppb) and Cd (3 ppb) standard solutions were carried out, in the some laboratory, the same day, on the same equipment, by the same laboratory personnel and by the same method. The repeatability was expressed as relative standard deviation (represented in Fig. 1).

Table 7

The computation of F_{calc} values and the comparison of these with F_{crit} value

Element	S_b^2	S_w^2	F_{crit}	$F_{calc} = S_b^2 / S_w^2$	Situation
Ni	6.095	1.025	2.62	5.95	$2.62 < 5.95$
Pb	0.572	0.133	2.62	4.30	$2.62 < 4.30$
Cd	0.276	0.054	2.62	3.55	$2.62 < 5.11$

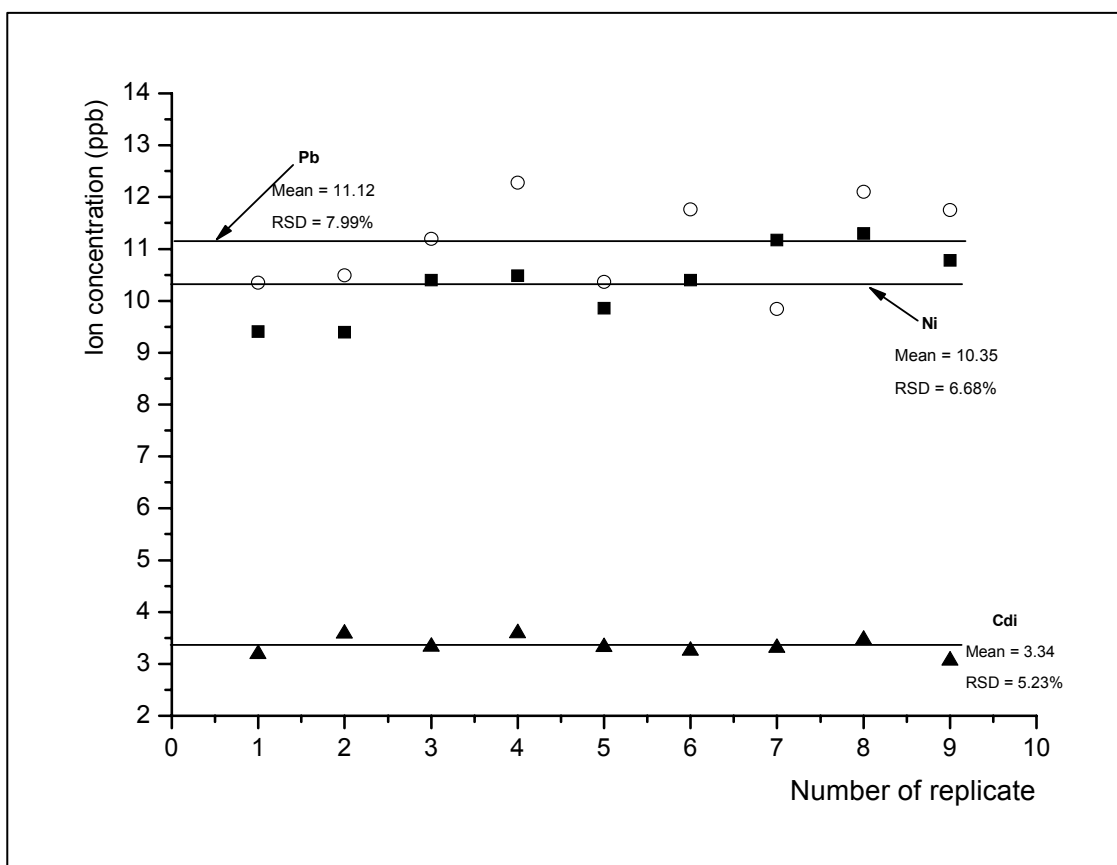


Fig. 1 – Graphical representation of the repeatability study.

The estimated values of uncertainties for the metals concentrations measurement were established based on uncertainty calculus used for the method validation for the measurement of analytes Ni, Pb, Cd from polyether polyols.

Introducing these data in equation (8) and assuming a value $t = 2$ for t-Student distribution, in the case of normal distribution of results, the number of samples necessary to be measured n_s was calculated (Table 8).

Table 8

The calculus of necessary number of samples to be analyzed for every analit

Analit	RSD %	u%	n _s
Ni	6.68	6.4	4.4
Pb	7.99	7.2	4.9
Cd	5.23	5.6	3.5

Because the calculated number of samples necessary to be measured n_s is a fraction, in practice it is recommended to choose in calculus the round number following the calculated fraction.

In the study of the method validation, the linearity range is a key parameter that must be determined. In this way, after the preliminary working range was established, the values of

absorbance for 10 standard solutions in the linearity range were measured. The x_i concentrations of the standard solutions were chosen to be distributed at equal distances over the linearity range. The homogeneity of variances was checked at the limits of working range. From the series of measurements 10 information values y_{ij} were obtained (Tables 9, 10, 11).

Table 9

Precision of AAS determinations of Ni

i	x_i (ppb)	$y_{i,1}$	$y_{i,2}$	$y_{i,3}$	$y_{i,4}$	$y_{i,5}$	$y_{i,6}$	$y_{i,7}$	$y_{i,8}$	$y_{i,9}$	$y_{i,10}$
1	2	0.025	0.025	0.0265	0.0229	0.0240	0.0226	0.0233	0.0217	0.0226	0.0199
2	4	0.041									
3	6	0.057									
4	8	0.073									
5	10	0.091									
6	12	0.109									
7	14	0.120									
8	16	0.137									
9	18	0.153									
N=10	20	0.171	0.1627	0.1617	0.1665	0.1665	0.1691	0.1636	0.1633	0.1636	0.1606

Table 10

Precision of AAS determinations of Pb

i	x_i (ppb)	$y_{i,1}$	$y_{i,2}$	$y_{i,3}$	$y_{i,4}$	$y_{i,5}$	$y_{i,6}$	$y_{i,7}$	$y_{i,8}$	$y_{i,9}$	$y_{i,10}$
1	2	0.101	0.1150	0.1147	0.1079	0.1096	0.0909	0.1001	0.1117	0.0864	0.1128
2	4	0.174									
3	6	0.245									
4	8	0.320									
5	10	0.375									
6	12	0.400									
7	14	0.468									
8	16	0.543									
9	18	0.597									
N=10	20	0.661	0.6570	0.6680	0.6570	0.6563	0.6243	0.6237	0.6330	0.6360	0.6160

Table 11

Precision of AAS determinations of Cd

i	x_i (ppb)	$y_{i,1}$	$y_{i,2}$	$y_{i,3}$	$y_{i,4}$	$y_{i,5}$	$y_{i,6}$	$y_{i,7}$	$y_{i,8}$	$y_{i,9}$	$y_{i,10}$
1	0.5	0.026	0.0270	0.0230	0.0235	0.0245	0.0223	0.0224	0.0273	0.0260	0.0258
2	1.0	0.048									
3	1.5	0.072									
4	2.0	0.095									
5	2.5	0.127									
6	3.0	0.141									
7	3.5	0.167									
8	4.0	0.190									
9	4.5	0.201									
N=10	5.0	0.227	0.2250	0.2290	0.230	0.2258	0.2272	0.2271	0.2171	0.2248	0.2240

The two levels of concentration x_1 and x_{10} were used in the calculation of variances s_1^2 and s_{10}^2 according to the equation:

$$s_i^2 = \frac{1}{n_i - 2} \sum_{j=1}^{10} (y_{i,j} - \bar{y}_i)^2 \quad (11)$$

Afterwards, the variances were tested (F test) to determinate the relation between these two limits of the working range. Then, the F_{calc} values with F_{crit} value from the F-distribution table were

compared. After checking the table with critical values F_{crit} of F distribution for $f_1 = f_2 = n - 1 = 9$ degrees of freedom and 99% confidence level, $F_{(9; 9; 0.99)} = 5.35$ was obtained.

After comparing the F_{calc} values calculated for each of the elements Ni, Pb, Cd with the F_{crit} value from the table, we may conclude that there is a random difference between the checked variances, those two populations having equal variances (Table 12). So, the linear calibration function is suited.

Table 12

The computation of F_{calc} values and the comparison with F_{crit} value

Element	s_1^2	s_{10}^2	F	$F_{calc} = s_{10}^2 / s_1^2$	Case
Ni	0.0000035272	0.000011052	5.35	3.26	$3.26 < 5.35$
Pb	0.00010157	0.00034639	5.35	3.41	$3.41 < 5.35$
Cd	0.0000035551	0.000012604	5.35	3.55	$3.55 < 5.35$

CONCLUSIONS

In the case of the quantitative determination of hazardous metals Ni, Pb, Cd from polyether polyols, the study of variance analysis was proved to be very useful. The variance of the sampling method is significantly bigger than the variance of the analysis method. This involves supplementary measures that should be taken by the analyst. These measures involve a better homogenization of product before collecting the samples and taking a sufficient number of samples so that the reported results are as close to reality as possible.

Based on the study of variance analysis the number of samples necessary to be collected was also established, in contrast with taking only one sample when the result obtained is inconclusive regarding the characteristics of the measured material.

By applying the F-test it was proved that in the case of the quantitative determination of Ni, Pb, Cd from polyether polyols by Atomic Absorption Spectrometry with graphite furnace, the utilization of a linear calibration function is suited for the chosen working range.

REFERENCES

- M.A. Linne, Atomic Spectroscopy (Chapter 8), in Spectroscopic Measurement, Edited by M.A. Linne, Elsevier, Amsterdam, 2002, p. 167.
- R.Q. Aucelio, R.M. de Souza, R.C. de Campos, N. Miekeley and C.L. Porta da Silveira, *Spectrochim. Acta, Part B: Atomic Spectroscopy*, **2007**, 62, 952.
- B. Salih, O. Celikbicak, S. Doker and M. Dogan, *Anal. Chim. Acta*, **2007**, 587, 272.
- M.G.A. Korn, D.S.S. dos Santos, B. Welz, M.G.R. Vale, A.P. Teixeira, D. De Castro Lima and S.L.C. Ferreira, *Talanta*, **2007**, 73, 1.
- *** SR 13251: 1996, "Vocabular internațional de termeni generali în metrologie".
- G. Kateman and L. Buydens, "Chemical Analysis, Quality Control in Analytical Chemistry", John Wiley & Sons, 1993, vol.60.
- J.C. Sherlock, W.H. Evans and J.J. Hislop, *Chem. Br.*, **1985**, 21, p.1019.
- P.C. Meier, R.E. Zund, "Statistical methods in analytical chemistry", 2nd Edition, J. Wiley & Sons, New York, 2000, p. 1-40.
- J. Mandel, "The statistical analysis of experimental data", Interscience Publ., J. Wiley & Sons, New York, 1964.
- *** ISO 8466-1: 1999 - "Calitatea apei, Etalonarea si evaluarea metodelor de analiza si estimarea caracteristicilor de performanta. Partea 1: Evaluarea statistica a functiei liniare de etalonare".
- U. Graf, H.J. Henning and K. Stange, "Formulae and tables of mathematical statistics", 2nd Edition, Springer Verlag, Berlin, Heidelberg, New York, 1996.
- L. Sachs, "Methods for statistical evaluation", 2nd Edition, Springer Verlag, Berlin, Heidelberg, New York, 1971.
- I. Tanase, A. Pana, G. L. Radu, M. Buleandra, "Validarea metodelor analitice", Editura Printech, Bucuresti, 2007, p. 245.
- D. Ceausecu, "Utilizarea statisticii matematice in chimia analitica", Ed. Tehnica, Bucuresti, 1982, p. 211-220.
- J. Emer, J.H. McB. Miller, "Method validation in pharmaceutical analysis. A guide to best practice", J. Wiley - VCM Verlag GmbH & Co. KGaA, Wienheim, 2005, p. 80.
- *** ASTM D 1452 : 1996, "Standard practice for preparation of calibration solutions for spectrophotometric and for spectroscopic atomic analysis".
- E. Cordos, C. Manoliu, "Spectrometria de absorbtie si de fluorescenta atomica", Editura Academiei RSR, p. 130, 143, 145.
- I. Tanase, "Analiza instrumentala, Tehnici si metode spectrometrice", Partea II-a, Editura Universitatii din Bucuresti, 2007, p. 85, 135.