FTIR ANALYSIS IN INDUSTRIAL POLLUTION MONITORING: THE ASSESSMENT OF THE METHOD PERFORMANCES USING AMIQAS COMPUTER PROGRAM

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abstract: In this research, it was developed a FTIR method to measure silica occupational exposure in workplaces airborne and the reliability of this method was studied by Amiqas computer program. A Shewhard control chard was performed in order to assume that the method is in statistical control. Also, it was calculated the method evaluation function which is based on a linear square regression analysis and this showed that the method is precise and without systematic errors. The relative mean square error was 5.5% and the analysed data were normally distributed. Using this method, various workplaces from some industrial technological processes were investigated. Authors conclude that FTIR method for determination of silica concentrations in occupational environment is in statistical and analytical control.

Introduction

A result of a measurement is unacceptable and may even be misleading if the quality of the method of measurement is not declared. Unfortunately, it is impossible to produce errorless data, but it is possible to produce data so that the uncertain can be estimated. Hence, the analytical methods employed should be statistically validated with respect to random and systematic errors in order to assess its reliability. It may be appropriate to document the quality and performance of a method of measurement and documentation is obtained by internal and external quality control. Quality control procedures ensure that the analytical method stays in statistical control with acceptable performance for longer periods of time. Internal quality control procedures ensure that the analytical method stays in statistical control, the uncertainty of measurement of the method is below the established value and alterations in the analytical performance do not appear. Because Shewhart control charts are sensitive to extreme analytical results, this type of control chart is conveniently used in the internal quality control. Shewhart control charts employed in connection with special decision rules, as for ex. Wheeler rules, may detect systematic errors. External quality control procedures ensure that the laboratory may document traceability and it likewise opens for the possibility to compare with other analytical methods, as well as it is a tool for

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Analele Universității din București – Chimie, Anul XV (serie nouă), vol. I, pag. 77-82

improving a method. For this purpose, the computer program AMI-Quality Assessment Scheme (AMIQAS) was especially designed to execute an easy statistical management of measurement data in relation to quality assurance [1]. The program is designed in accordance to international guidelines and recommendations [2]. Taking into account these considerations, we developed a FTIR method for the monitoring of silica industrial pollution and we used Amiqas computer program in order to assess the reliability of this method.

Experimental

Air samples with a flow rate of 4.2 l/min. in working environment were collected using membrane filters with the pore size of 0.8 μm. The filters were inserted into closed cassettes; these cassettes were inserted into a preselector device (cyclone GK2.69) in order to separate dust respirable fraction (this fraction contains particles having aerodynamic diameter below 10 μm) from all dust in occupational environment, in accordance with Romanian guidelines recommendations [3]. Personal samplers type Gillian HFS 113A (New Jersey Instrument Corp., USA) were used. The pumps were attached of selected worker's body, they being powered by batteries. Air samples were collected during entire work shift. After sampling, the filters were ashen in muffle furnace for 2 h at 800°C; sample ash was pressed into a KBr pellet using standard technique and analysed by Fourier transform infrared (FTIR) spectroscopy [4, 5].

A Fourier transform infrared spectrometer type Jasco 460 Plus was used. α-quartz mineralogical variety was analysed using 800 cm^{-1} analytical line. This band is originated from the symmetrical stretching vibration of Si-O-Si groups. As standard, Dorentrup DQ12 quartz, having a content of 87% α-quartz was used. Working range was between 0.025-.4 mg α-quartz/m^3 air for a volume of air of 0.4 m^3. Calibration curve was between 0.2-1.75 mg α-quartz. The base-line method was used for the calculation of the absorbance; the samples were scanned over 1000-600 cm^{-1}. A resolution of 4 cm^{-1} was used. The assessment of the performances of FTIR method used in this study was made. In this respect, we used the computer program Amiqas which is in accordance with the ISO guidelines [1,2]. For Amiqas evaluation, we prepared (by KBr disc technique) five quartz standard concentrations, covering the working range, namely: 0.22; 0.50; 1.00; 1.50; 2.00 mg α-quartz; we performed ten independent method runs on ten different randomly selected days. At each true concentration, duplicate measurements were performed. In order to assume that the method is in statistical control, the results were plotted in a Shewhart control chart in the order of appearance. In this control chart, the mean concentration measured in several control samples is plotted on the y-axis versus time on the x-axis. The results are accepted, if situated between statistically defined control limits (Wheeler); in this case, the method is in statistical control. If outside the control limits, the method is suspected to be out of control and the cause should be identified and corrected to re-establish control before measurements are continued. The evaluation of the analytical method is obtained by a plot method evaluation showing the measured concentrations versus the true concentrations. The method evaluation function (MEF), which is the expected value as a function of the conventional true concentration, is then estimated statistically. The square root of the relative mean square error ($RMSE^{1/2}$) was calculated for estimation of the uncertainty and systematic errors. Because standard samples were analysed with different frequencies, it was advantageous to display the normalised values by calculating the Z-scores for measurements. A Z-score is the difference between the control measurement and the mean value, divided by the standard deviation for the control material. Using this method, various workplaces from the following economic activities were investigated: manufacture of machine-tools (sand blasting, metal cleaning, coremaking and bench moulding), manufacture of basic metals (sand blasting, bench moulding, coremaking and metal cleaning), ore extraction (quarry and marble) and manufacturing of refractory materials (raw material transport and raw material pressing). In order to test the interferences due to various minerals, the qualitative phase analyse of the raw materials from the investigated workplaces was performed by X-ray powder diffraction. In the case of the presence of a significant amount of calcite (over 20% of the total dust), the filters were washed with 9% w/w hydrochloric acid. Cristobalite and tridimite were not encountered in the investigated samples. X-ray diffraction technique showed that kaolinite was removed during muffle furnace ashing procedure.

Results and Discussion

Fig. 1 illustrates Shewhart control chart of the silica measured residual concentrations versus the true concentrations (the center line).

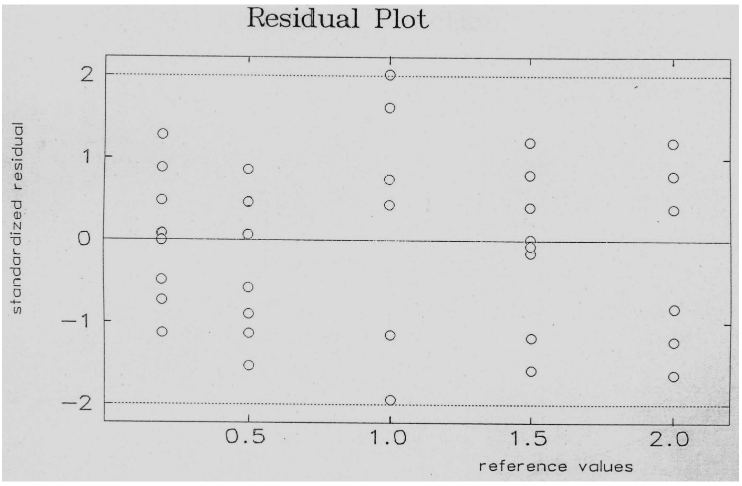

Fig. 1 *Shewhart control chart*

It can observe that, the control chart contains a center line, representing the target value (which the control measurements in average should hit, when the method is in statistical control) and control chart limits arranged symmetrically around and parallel with the center line. Around the center line there are plotted the measured standard values $\pm 2\sigma$ (σ-standard deviation); a part of these values were eliminated in accordance with statistical rules used by the program. As is shown in Fig. 1, the measured standard concentrations are inside the 2σ limits, in accordance with the Wheeler rules used by the program, the method being in statistical control (the measured standard concentration are distributed around the centre line). In Fig. 2 is shown the method evaluation function (MEF) which is based on a linear least square regression analysis of the measured standard concentrations (Y) versus the true concentration (μ), i.e. MEF(μ)=$\beta\mu+\alpha$, where β is the slope and α is the intercept. In our case, MEF(μ)=1.0060μ+0.0360; this means that β=1.006≈1, which shows that the method is precise and without systematic errors.

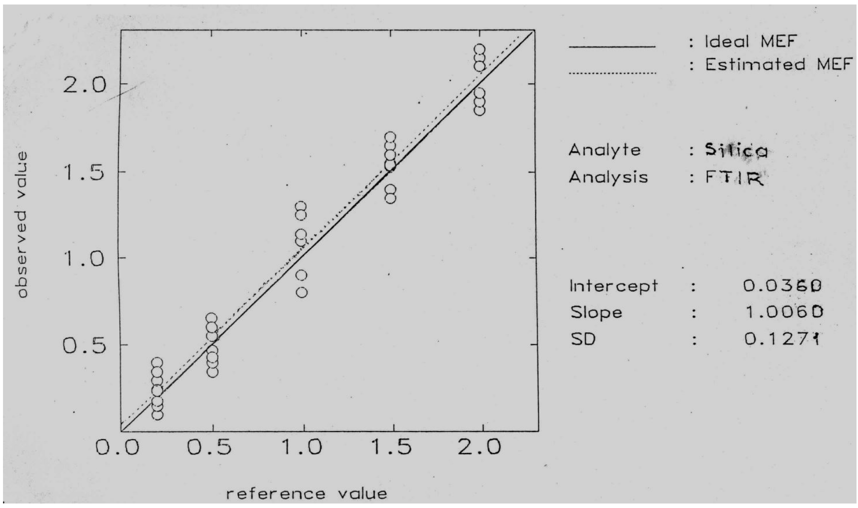

Fig. 2. *Method evaluation function*

The square root of the relative mean square error (RMSE$^{1/2}$)has been used for the simultaneous estimation of the uncertainty and systematic errors. RMSE$^{1/2}$ values were calculated and plotted versus the true concentrations (Fig. 3). An uncertainty of 10% is accepted. From Fig.3 it results that SD=0.055<1 and this means that the relative mean square error is below 10%, namely 5.5%. In Fig. 4 are presented N-score values plotted versus the measured standard values (and distributed inside the 2σ limits). N-score ,Φ, is given by the function: $\Phi=4.9[p^{0.14}-(1-p)^{0.14}]$, where p is the probability that the measured value it is equal with the true value; $p\in[0,1]$.We can see that N-score values are distributed on a straight line and this means that the measured values have a normal distribution. N-score correlation coefficient, ρ, has the value of 0.9812≈1 and this means also a normal distribution of the measured values.

Using this method we investigated the presence of silica in the workplace airborne of various technological processes (s. Table 1).

We think that the data reported in the Table 1 may be regarded as representative of the average ambient situation because of several environmental, methodological, technical and analytical parameters. The analysis of silica concentrations in the investigated workplaces suggest the existence of a higher health risk in workers from manufacture of machine-tools and basic metals in comparison with ore extraction or manufacture of refractories.

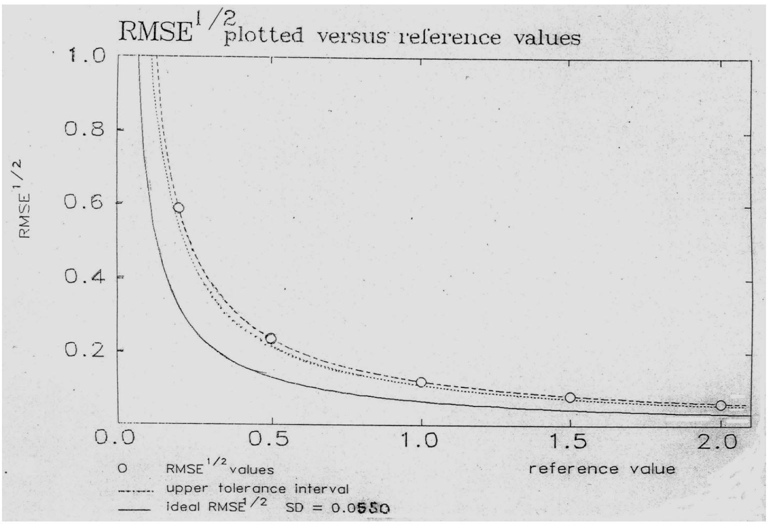

Fig. 3: RMSE$^{1/2}$ values and the upper tolerance limit versus the true value of quartz

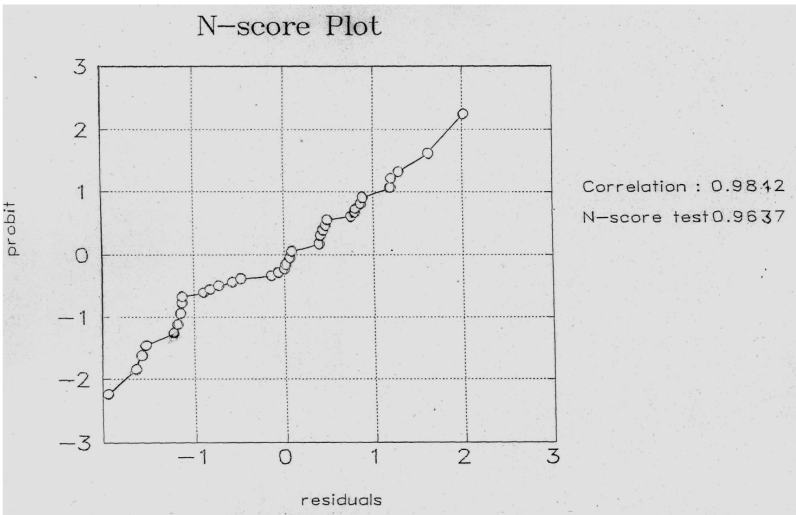

Fig. 4 *N-score values*

Table 1. α-cuartz concentrations in occupational environment in various technological processes

No	Industry	Workplace	α-cuartz concentrations (mean values)(%)
1	Manufacture of basic metals	Sand blasting	65
		Bench moulding	41
		Coremaking	46
		Metal cleaning	20
2	Manufacture of machine-tools	Sand blasting	71
		Bench moulding	38
		Coremaking	59
		Metal cleaning	43

No	Industry	Workplace	α-cuartz concentrations (mean values)(%)
3	Ore extraction	Marl extraction	15
		Quarry extraction	30
4	Refractory material manufacture	Raw material transport	21
		Pressing raw materials	18

Conclusions

We can conclude that FTIR method developed in this study proved to be sensitive and reliable. The assessment of the method performances by Amiqas computer program has shown that the method is in statistical and analytical control. The method evaluation function, which is based on a linear square regression analyse, has shown that the method is precise and without systematic errors. The method has been successfully used to measure silica concentrations in the occupational environment.

REFERENCES

1. ***World Health Organization. Regional Office for Europe (1993) *Training Manual on Basic Elements of Quality Assurance / Quality Control*, 3-50.
2. Christensen, J.M. (1992) *J. Anal. Atom. Spectroscopy* **7**, 329-35.
3. ***Ministerul Muncii si Solidaritatii Sociale. Ministerul Sanatatii si Familiei (2002) *Norme Generale de Protectie a Muncii*, 388.
4. Stanescu Dumitru, R., Branisteanu, R., Peter, K., Oros, C., Sirb, L. şi Pribu, M. *Metode de referinta pentru masurarea concentratiei agentilor chimici si fizico-chimici in mediul profesional*, CD, Editura PIM, Iasi.
5. Mandravel, C. şi Stanescu Dumitru, R. (2003) **Metode fizico-chimice aplicate la masurarea noxelor in mediul profesional,** Editura Academiei Romane, Bucuresti, 56-60