

ELEMENTAL COMPOSITION OF DUST IN A MANURE FOUNDRY AS  
DETERMINED BY EDXRF AND NAA<sup>+</sup>

BY

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ABSTRACT

Few data are available on the inorganic atmospheric pollution in the manure foundries. Therefore, the elemental composition of atmospheric aerosol was investigated for ten sites in the manure foundry, in the industrial area, Kafer El-Ziat, Egypt.

Total aerosol samples were collected with ORTEC 302 Portable Air Samplers Collector. During a ten week period, with personal samples carried by staff active in different department of the foundry, a survey was made of the level. Some samples were also taken of the major emission sources in the foundry. All samples were analyzed by energy dispersive X-ray fluorescence (EDXRF) and reactor neutron activation analysis (RNAA). About 23 elements were quantified in all cases by RNAA. The major elements of these matrices, Si, P, S, and I do in fact not produce intensive  $\gamma$ -emitting radioisotopes after neutron irradiations, they were quantified by EDXRF. The neutron-induced nuclides were analyzed by  $\gamma$ -ray spectrometry. By varying the neutron flux and the time of irradiation we were able to detect the following elements, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Cu, Zn, Ca, As, Br, Rb, Sr, Mo, Cd, In, Sn, Sb, I, Ba and La.

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### INTRODUCTION

The hazard of suspended particulate matter in workplace atmospheres is often evaluated solely in terms of total dust concentrations in the air. Obviously also the particle size, which determines the penetration into and retention by the human respiratory system, and the concentration of the individual elements are prime considerations for evaluation of occupational exposure.

A workplace of a manure foundry is in fact a multi-source area of particulate contaminants. Owing to the variety of sources in such an area the nature of particulates suspended in the air varies considerably in chemical composition. For the elemental analysis of the particulate matter collected, instrumental neutron activation analysis is still one of the methods of choice, because of its sensitivity for most of elements of interest, its precision and negligible contamination risk and above all because it does not require dissolution of the samples.

#### Theory

The theory of neutron activation analysis is simple [1-3]. The method is based on the principle that when materials are irradiated in a nuclear reactor with thermal neutrons (energy ca. 0.025 eV) or in another neutron source, some of the atoms present are converted into radioactive isotopes. About 70 elements of the periodic table include nuclides which possess activation and decay properties suitable for thermal neutron activation analysis

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The most usual type of activation is  ${}^A_Z X (n, \gamma) {}^{A+1}_Z X$ . The newly formed nuclide is another isotope of the same element. The total number of radioactive atoms  ${}^+N$  of a particular nuclide is given by eqn. 1:

$${}^+N = \theta_{th} \sigma_o \left( 1 + \frac{\theta_{epi} I_o}{\theta_{th} \sigma_o} \right) \frac{N}{\lambda} S \quad \dots\dots (1)$$

where  $\sigma_o$  is the cross-section for the  $(n, \gamma)$  reaction with thermal neutrons (unit : 1 barn =  $10^{-24}$  cm<sup>2</sup>),  $I_o$  the activation neutron integral (unit : barn),  $\theta_{th}$  the thermal neutron flux (n cm<sup>-2</sup> s<sup>-1</sup>),  $\theta_{epi}$  the epithermal neutron flux (n cm<sup>-2</sup> s<sup>-1</sup>),  $N$  the number of atoms of a certain nuclide ( $= 6.10^{23} p\phi g/A$ ), ( $p$  = % element in the compound,  $\phi$  = isotopic abundance of the target nuclide,  $g$  = weight of the compound;  $A$  = atomic weight of the element),  $\lambda$  the disintegration constant ( $\lambda = 0.693/t_{1/2}$ ;  $t_{1/2}$  = half - life of the radioactive isotope), and  $S (= 1 - e^{-\lambda t})$  the saturation factor ( $t$  = irradiation time). The type and energy emitted by the radioactive isotope and the decay rate are specific identifying characteristics. A quantitative analysis can be made by comparing the element's radioactivity in the sample with that of a suitable standard, irradiated simultaneously or through the intermediate of flux monitors [3]. It is assumed that all the parameters ( $\phi$ ,  $\sigma$ ,  $\theta$ ,  $t$ , counting efficiency) remain identical for the unknown and the standard and that the radionuclide is not formed from another nuclide in the sample (i.e no nuclear interference) [4-7]. NAA is the more

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interesting when the radionuclides formed are  $\gamma$ -emitters, since measurement with a HP-Ge detector allows high resolution - spectrometry. This promoted instrumental neutron activation analysis (INAA) on a large scale, further promoted by the development of appropriate computer software for automatic data reduction and information.

EDXRF analysis

X-ray fluorescence spectrometry (XRF) of one of the most convenient and widely used techniques for the analysis of trace amounts in atmospheric particulate. It requires little or no sample preparation, is non-destructive, and provides a rapid analysis. The spectra were analyzed for 24 elements by using a simple net peak area determination and applying correction for interfering spectral lines ( $k_B - k$ ) overlap of neighboring elements. The common problem then is to obtain reliable net peak areas for the individual characteristic X-ray lines in the spectrum. To deal with the very complex nature, in particular, of the photon X-ray spectra, the deconvolution method is based on the powerful nonlinear least squares optimization algorithm of Marquardt [8]. However, in using this nonlinear - fitting principle one must overcome several problems normally associated with the method. The major problems are the number of parameters in the fitting function, the accuracy of the model used, and avoidance of the selection of physically meaningless minima in the X-hypersurface.

The first two problems require the use of a suitable fitting function. The model used consists essentially of

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two cumulative portion : the background function and the function representing the characteristic X - ray spectrum. The background is built up of different components, depending on the excitation mode. In mono-energetic photon excitation the background originates in the detector itself and results from incomplete charge collection of the high energetic excitation X- rays which interact with the detector after scattering onto the sample [9].

As a description of the background for all excitation modes, the following relation is used:

$$\text{BACK}(E) = \sum_{i=0}^{n1} B1i (E - E_0)^i + B20 \exp\left[\sum_{j=i}^{n2} B2j(E - E_0)^j\right] + B30 \exp\left[\sum_{k=i}^{n3} B3k(E - E_0)^k\right] \cdot \text{ABS}(E) \dots\dots\dots (2)$$

in which E is the energy and E<sub>0</sub> a suitable reference energy. The first term is used to describe the background when only a small energy interval is fitted; for larger fitting regions, when the exponential terms are included in the description, only B10 is retained. The second term represents the background not affected by absorption (n<sub>2</sub> = 3). The third term is the bremsstrahlung background, which is affected by an absorption factor ABS(E).

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Normally for a number of spectra originating from a group of similar samples, the parameters  $B_{2j}$  for  $j > 0$  and  $B_{3k}$  for  $k > 0$  are determined once from one or more representative spectra. These parameters are then kept constant for the remaining spectra in the set. In this way only three background parameters  $B_{10}$ ,  $B_{20}$ , and  $B_{30}$  are to be optimized.

The second part of the fitting function describes the entire X - ray line spectrum. The emission spectrum of an element consists of a number of X - ray lines; each line is, at a first approximation, represented by a Gause function:

$$G(x,n,m) = \frac{1}{\sqrt{2\pi} W_{n,m}} \exp\left(-\frac{(P_{n,m} - X)^2}{2W_{n,m}^2}\right) \dots\dots\dots (3)$$

where  $W_{n,m}$  is the width of the peak number  $m$  of element  $n$ ,  $P_{n,m}$  the position of the peak number  $m$  of element  $n$ ,  $x$  the channel number, and  $W_{n,m}$  and  $P_{n,m}$  are calculated from the relations:

$$P_{n,m} = C_1 + C_2 E_{n,m} + \exp(-C_3 E_{n,m}^2) \dots\dots\dots (4)$$

$$W_{n,m}^2 = C_4 + C_5 E_{n,m} \dots\dots\dots (5)$$

where the  $C_i$  are the spectrum calibration parameters and  $E_{n,m}$  is the energy of line  $m$  of an element  $n$ . This formulation mean that in the optimization it is not the individual position and width of every peak that is determined, but only the position ( $C_1 - C_3$ ) and the resolution ( $C_4 - C_5$ ) calibration parameters

of the entire spectrum. The term between brackets in Eq. (4) can be used to account for the nonlinearity of the calibration in the low- energy part of the spectrum.

The X- ray emission of an elements is then modeled with a single area parameter and the various transitions are scaled to this area by the use of known relative intensities, therefore the fitting function becomes:

$$YFIT = BACK(E) + \sum_n A_n \left[ \sum_m G(x, n, m) \cdot R_{n,m} \cdot ABS(E_{n,m}) \right] \dots\dots\dots(6)$$

The first summation concerns the number of elements ;  $A_n$  is proportional to the number of photons emitted towards the detector. The second summation runs over the number of lines for each elements;  $R_{n,m}$  is the relative transition probability.  $ABS$  is the absorption factor for a particular X - ray with energy  $E_{n,m}$ . The data are smoothed, normalized to the intensity of the main peak  $k_{\alpha}$ , and stored together with calibration of the original spectrum. The correction term  $S_n(x)$  for intense peaks in each spectrum is calculated by use Eq.(5) and multiplied by the number of  $K_{\alpha}$  photons detected. The total spectrum function thus becomes:

$$YFIT = BACK(E) + \sum_n A_n \left[ \sum_m G(x, n, m) \cdot R_{n,m} \cdot ABS(E_{n,m}) + S_n(x) \cdot R_{n,1} \cdot ABS(E_{n,1}) \right] \dots\dots\dots(7)$$

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The last factor to be discussed is the absorption term ABS(E). Since the methods are mostly used for the determination of trace constituents in low - Z matrices absorption edges can be neglected in the calculation of the absorption due to the sample and the X - ray absorption coefficient can be described as:

$$\mu(E) = aE^b \quad \dots\dots\dots(8)$$

whereas , absorption is mostly due to the sample itself , with (at low energies) a contribution from the detector beryllium window, the gold contact, and the silicon dead layer.

The third problem, avoiding the selection of undesired minima in the  $\chi^2$  - surface, is dealt with by redefinition of the  $\chi^2$  - function [10]:

$$\chi^2 = \frac{1}{\nu} \sum_i \left[ \frac{(Y_i - Y_{FITi})^2}{\sigma_i^2} + \sum_j \frac{(A_j - A_{opj})^2}{\sigma_{A_{opj}}^2} \right] \dots\dots(9)$$

The first term is the normal  $\chi^2$ - function. The second term is added to enhance the curvature of the  $\chi^2$  - surface when the fitting parameter  $A_j$  reaches values strongly different from the expected value  $A_{opj}$ . The range for each parameter is controlled by  $\sigma_{A_{opj}}^2$  ;  $A_j$  denotes the calibration and absorption parameters.



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## EXPERIMENTAL

### Sampling

The aerosol sampling was carried out at the workplaces of a manure foundry, in the industrial area, Kafer El-Ziat, El-Gharbia, Egypt between March 29 and June 24, 1989. The airborne particulate matter was collected on 400 cm<sup>2</sup> Whatman filter paper, using ORTEC 302 Portable Air Filter Sample Collector. Air was drawn continuously through the samplers at a flow rate of 0.8 m<sup>2</sup>.h<sup>-1</sup>., and the filters were changed six times a week, a sampling period of 1.5 hr at about 12 a.m. was necessary, corresponding to a volume of about 1.2 m<sup>3</sup> of air during an hour day. Simultaneously, wind direction, air pressure and relative humidity were recorded at 1.6 m above ground level.

### Analysis

After weighing at constant temperature and humidity (50% RH) the filter were pressed into pellets for INAA. The procedure followed was similar to that of Schutyser et al [6] and involved 2 separate irradiations with subsequent measurement of short - and longlived product radionuclides by means of a large HP-Ge detector.

Concentrations of total suspended particulate matter were obtained by weighing filters before and after aerosol collection.

All samples were re-analysed by an energy dispersive X - ray Fluorescence analyzed with interelement corrections. Twenty seven element were typically measured by these two

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methods. Full details about the experimental EDXRFA procedures were given elsewhere [7,8].

The overall blanks were most significant for Na, Al, Cl, K, Ca, Cr, Fe and Zn but were not prohibitive for the analysis of the particulate collected. Up to 27 elements could generally be determined, often with precisions better than 10% or even better than 5% for Al, Mn, Na and Fe.

#### RESULTS AND DISCUSSION

In table. I the average concentrations for twenty seven elements as measured at all indoor department are given. From the comparison with the concentrations at the outdoor it is clear that intense emission sources exist in the foundry for eight elements and are only 2 to 4 times higher than the outside air values.

To illustrate the concentration gradients in the workplaces the maximum and minimum time-averaged concentrations are also given.

The concentrations of airborne trace elements, agreed fairly well for each of the sampling periods. This indicates that the air inside the workplace was well mixed. On the other hand, dramatic changes in ambient concentrations were noted as a function of time (sampling number). This is demonstrated in Fig(1), which shows concentrations of 6 elements for sampling periods N1 through N7. The variability is particularly large

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for Si and Mg, but the high Mg concentration observed for sample N2 may be related to rather abnormal activities inside the foundry. Fig. (1) also indicates that the variation with time was not the same for all elements ; e.g. the highest Zn levels were obtained for sample N3, when Mg, S and Cu were lowest. The concentrations of the various elements were generally poorly correlated, and the interelement ratio (and thus the comparison of the suspended particulate matter) changed significantly as a function of time.

Mean concentrations of airborne trace elements inside the workplace, obtained by averaging the total filter results over the different sampling periods, are given. The table also contains mean concentrations for outside air during March to June 1989.

The different sources on the air quality in the workplace can also be evaluated by comparing the composition of the dust at the sampling sites with the composition of some of the materials handled or produced in the foundry. Similarities or dissimilarities between sample compositions constitute useful information about the spread of pollutants from a single source or several sources generating pollutants similar in composition.

The result of this classification is given in Fig.(2). This figure show that the elements concentrations are directly related to pollution sources. We can see that the highest

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concentration nearly at zero point.

#### CONCLUSIONS

From these experiments a number of conclusions have been drawn, that may be useful in analogous situations. The sampling experiments can be used to measure the concentration levels in the workplace to within 10% and pinpoint the major source areas. It can only give an estimate of the personal exposure to the worker, at a distance of intense sources of coarse particles. A realistic estimation of personal exposure requires anyhow longterm or frequent sampling, with personal samplers or with stationary.

It was further shown that instrumental neutron activation analysis and energy disperse X - ray fluorescence can be a powerful tool in the study of the composition of industrial particulate matter.

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TABLE 1: MEAN, MAXIMUM AND MINIMUM CONCENTRATIONS OF ELEMENTALS  
(ng.m<sup>-3</sup>) MEASURED INSIDE AND OUTSIDE THE FOUNDRY

Element	concentration					
	inside				outside	
	NAA		EDXRF		Both Tech.	
	Maximum	Minimum	Maximum	Minimum	Geom.Mean(s.d)*	Geom.Mean(s.d)
Na	110000	13452	90133	11000	52000(3.1)	45650 (2.4)
Mg	63499	20800	65500	21347	31200(2.9)	490 (2.0)
Al	150800	36790	112543	31670	61600(3.4)	66700 (2.1)
Si	-	-	13210	4320	5640(2.7)	190 (2.3)
P	-	-	890	360	380(2.9)	126 (1.4)
S	-	-	12400	5880	6900(1.8)	1866 (1.3)
Cl	100897	26780	107000	27966	50000(2.9)	46600 (2.3)
K	80000	38976	69987	36000	43000(1.8)	10850 (2.9)
Ca	150300	43122	143211	42000	80000(2.5)	1181 (2.7)
Ti	93	78	88	83	85(2.4)	89 (3.5)
V	2.5	0.73	-	-	2.1(1.7)	2.4 (3.6)
Mn	48.7	14.9	23.8	10.7	16.19(3.2)	15.3 (1.9)
Cu	24.0	570	1560	350	720(2.7)	38 (1.9)
Zn	6113	990	7200	1234	1840(3.9)	78.5 (4.5)
Ga	1.5	0.17	1.2	0.13	0.35(1.8)	0.5 (1.7)
As	1.6	0.19	-	-	0.43(2.4)	0.36 (1.9)
Br	10.1	2.3	7.9	1.8	3.45(2.9)	2.66 (2.88)
Rb	33.8	8.9	35.5	6.82	11.33(3.8)	9.82 (3.1)
Sr	52.7	10.1	35.2	5.91	13.00(2.5)	9.71 (2.3)
Mo	1.95	0.53	1.12	0.40	0.71(3.2)	0.72 (2.1)
Cd	5.32	0.61	5.71	0.68	1.38(4.0)	1.48 (1.7)
In	0.018	0.004	0.015	0.003	0.006(3.0)	0.007 (1.7)
Sn	78.3	14.9	62.1	13.2	21.29(3.1)	18.42 (3.3)
Sb	0.2	0.11	0.4	0.1	0.16(3.1)	0.14 (2.5)
I	2.39	0.42	2.4	0.33	0.62(2.8)	0.77 (2.6)
Ba	37.0	13.8	26.9	10.7	18.7(2.1)	14.6 (2.5)
La	0.76	0.23	0.43	0.21	0.32(2.0)	0.48 (3.1)

\* - % relative standard deviation error

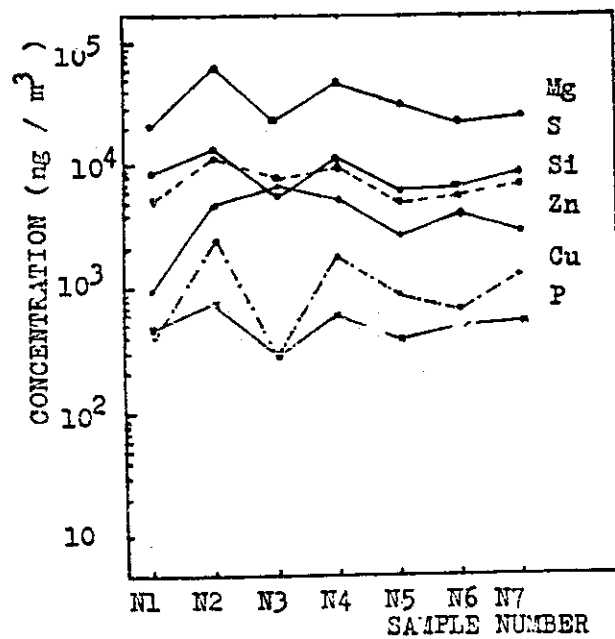
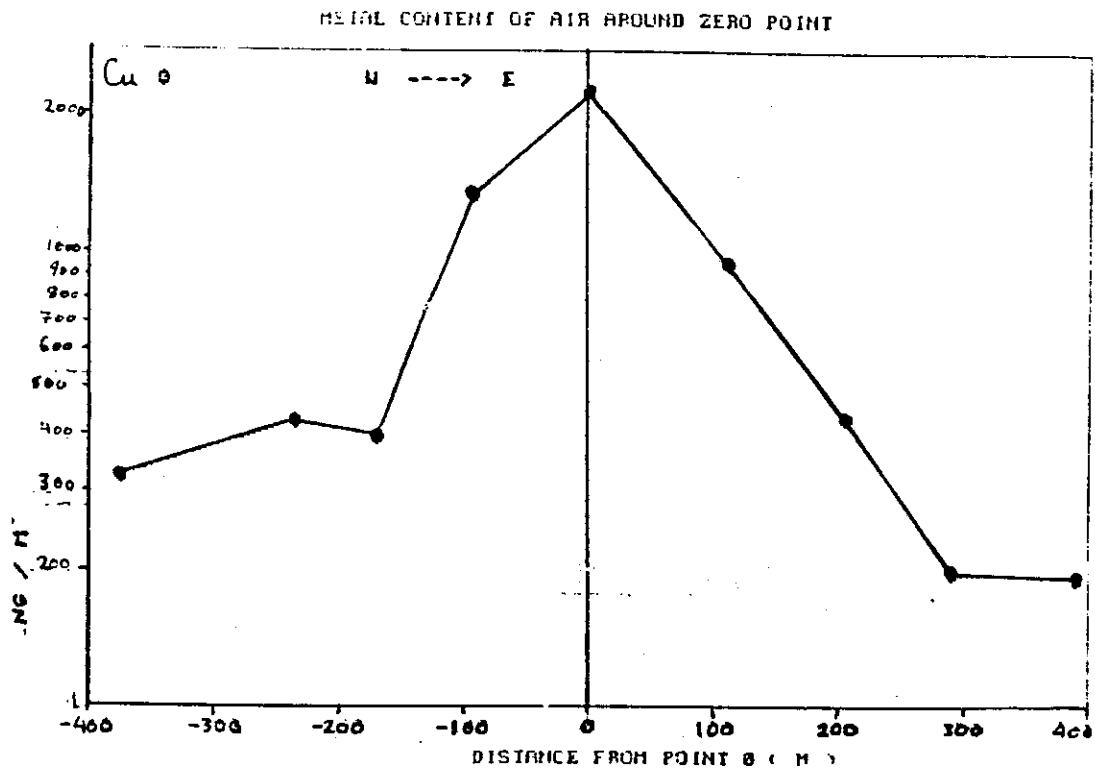


Fig.1.: Concentrations of 6 Elements in The Air of The Workplace during sampling periods N1 Through N7.

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التركيب العنصرى للغبار فى مصنع لاسمدة وتم تعيينه  
باسلوب NAA, EDXRF

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تم فى هذه الدراسة قياس التركيب العنصرى للغبار فى مصنع الاسمدة بمدينة كفر الزيات - محافظة الغربية- مصر حيث تم جمع عينات يوميا وخلال ساعات العمل بالمصنع لمدة عشرة اسابيع وذلك باستخدام جامع للعينات حيث تم اختيار عشرة اماكن مختلفة فى ارجاء المصنع. جميع العينات تم تحليلها باستخدام اسلوبى التقنية التحليل التنشيطى بالنيوترونات وطريقة اشعة اكس الانبعاثية وهما طريقتان حساستان وتكمل كل منهما الاخرى لزيادة عدد العناصر التى يمكن الكشف عنها حيث تم تعيين 27 عنصرا منها اربعة امكن تعيينها فقط باستخدام طريقة اشعة اكس الانبعاثية. وهى عناصر السليكون والفوسفور والكبريت واليود. فى حالة اسلوب التقية النووية ( NAA ) تم استخدام فيض مختلف للنيوترونات مع تعيير زمن التشعيع وذلك لزيادة عدد العناصر وحساسية الطريقة.