



HAL
open science

Control and correction of the sample absorption effect in the analysis of atmospheric aerosol by X-ray fluorescence spectrometry

I Chiapello, G. Bergametti, J.P. Quisefit, P de Chateaubourg

► To cite this version:

I Chiapello, G. Bergametti, J.P. Quisefit, P de Chateaubourg. Control and correction of the sample absorption effect in the analysis of atmospheric aerosol by X-ray fluorescence spectrometry. *Analisis*, 1997, 25, pp.141-147. hal-02327200

HAL Id: hal-02327200

<https://hal.science/hal-02327200>

Submitted on 22 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Control and correction of the sample absorption effect in the analysis of atmospheric aerosol by X-ray fluorescence spectrometry

I Chiapello, G Bergametti, JP Quisefit*, P de Chateaubourg

Laboratoire interuniversitaire des systèmes atmosphériques (LISA), universités Paris VII et Paris XII, URA CNRS 1404,
61, av du Général-de-Gaulle, 94010 Créteil cedex, France

Summary — X-ray fluorescence is an efficient method for quantitative elemental analysis of atmospheric aerosol assuming thin layer hypothesis. The major difficulty for this kind of sample is due to the possible absorption of the fluorescent radiation by the sample matrix. For this reason, we have experimentally determined the conditions of thin layer analysis for a set of aerosol samples collected in Cape Verde Islands, by applying an emission-transmission method, which consists of a measurement of the sample transmission using the 'radiator' technique to correct the absorption effect in relation to the concentrations for samples of intermediate thickness. From the experimental results, a linear relation has been established between the mass of matter present on the filter and the absorption coefficient for the tested elements (Fe, Ti, Ca, K, S, Si, Al). In a second step, the absorption coefficients are calculated by determining a matrix composition with previous absorption measurements. The thin layer analysis limits deduced from this calculation are in good agreement with those calculated from measurements. Furthermore, it allows an estimation of absorption effects for elements whose transmission has not been measured.

Résumé — Contrôle et correction de l'effet de matrice dans l'analyse d'aérosols atmosphériques par spectrométrie de fluorescence X La spectrométrie de fluorescence X est une méthode analytique élémentaire des particules atmosphériques prélevées sur filtre, qui repose sur l'hypothèse de la couche mince. La difficulté majeure est liée à la possible absorption de la radiation de fluorescence par la matrice de l'échantillon. Pour cette raison, nous avons déterminé expérimentalement les conditions de l'analyse en couche mince pour une série d'échantillons d'aérosols collectés aux Îles du Cap Vert, en appliquant la méthode d'émission-transmission, qui consiste en la mesure de la transmission de l'échantillon au moyen d'un « radiateur ». Pour les échantillons d'épaisseur intermédiaire, la méthode permet de corriger la concentration de l'effet d'absorption qui l'affecte. À partir des résultats expérimentaux, une relation linéaire a été établie entre la masse de matière présente sur le filtre et le coefficient d'absorption pour divers éléments testés (Fe, Ti, Ca, K, S, Si, Al). Dans une seconde étape, les coefficients d'absorption sont calculés en déterminant une composition de la matrice en accord avec les mesures d'absorption précédentes. Les limites d'analyse en couche mince déduites de ces calculs sont en bon accord avec ceux issus de l'expérience. De plus, une estimation des effets d'absorption est possible pour des éléments pour lesquels la méthode de transmission n'a pu être appliquée.

X-ray fluorescence / thin layer samples / aerosols / elemental analysis / emission-transmission method

Introduction

X-ray fluorescence spectrometry is now an analytical method currently used to perform elemental analysis of atmospheric aerosol samples collected on a filter [1]. It presents indeed many advantages: the sample is analysed without preliminary treatment, the analysis is fast and conservative, and it is possible to analyse in a satisfactory way a great number of chemical elements, especially sulphur, silicon, phosphorus and chlorine, all hardly accessible by other analytical methods.

However, the major difficulty with this technique results from the possible absorption effect by the sample matrix (or by the particle size itself) of the fluorescent radiation [2]. Indeed, the quantitative elemental analysis of aerosol by X-ray fluorescence is based on the hypothesis that the sample constitutes a thin layer. It means that neither the exciting beam, nor the fluorescent radiation, are disturbed by the atoms of the sample. It is only under this condition that the intensity of fluorescence is linearly proportional to the elemental mass deposit on the filter. In fact, this assumption of thin layer depends not only on the global composition of the sample, but also, for a given sample, on the analysed element. Hence, the matrix effect particularly affects light element analysis, since the weaker the energy of fluorescent radiation is, the more important is the absorption effect.

Up to now, the solution adopted has consisted in determining experimentally the threshold limits for each element beyond which the thin layer analytical condition becomes

unacceptable. This study has been carried out for standards representative of matrices currently observed for aerosols [1]. However, it is clear that the aerosol matrix is strongly variable from one sample to another, and consequently, to be rigorous, the thin layer hypothesis has to be checked for each sample type. This could be done in a theoretical way if the matrix composition was perfectly known, but it is rarely possible for atmospheric aerosol collections.

Therefore, the aim of this study was to determine experimentally the conditions of analysis of thin layer for a set of atmospheric aerosol samples collected in Cape Verde Islands. This is possible by applying the method developed by Leroux and Mahmud [3], which involves the measurement of the sample transmission, and allows us to take into account the absorption effect that disturbs the measured concentrations.

Dependence between fluorescent intensity and sample thickness

As described by Tertian and Claisse [4], the thickness of the analysed sample, relative to the quality of the analysis, may be considered in three regions: thin, intermediate or infinite thickness (fig 1). The infinite thickness intensity I_{∞} is dependent on the analysed wavelength and on the composition.

In order to define in a universal way these different cases of influence of the specimen thickness h on the fluorescent intensity I_h , the intensity ratio is used:

$$\frac{I_h}{I_{\infty}} = 1 - \exp(-k) \quad (1)$$

* Correspondence and reprints.

Received 22 January 1997; revision received 12 May 1997; accepted 16 May 1997.

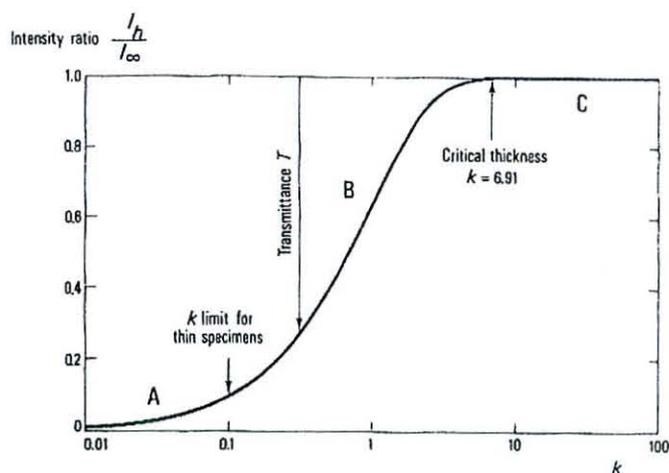


Fig 1. Intensity ratio I_h/I_∞ as a function of $k = \rho h \mu^*$.

$$\text{with } k = \rho h \left[\frac{\mu_{s,\lambda e}}{\sin \psi_1} + \frac{\mu_{s,\lambda i}}{\sin \psi_2} \right] = \rho h \mu^*$$

where ρ is the specimen density, μ^* the complex attenuation coefficient, ψ_1 and ψ_2 the characteristic angles of the analytical spectrometer, and $\mu_{s,\lambda e}$ the massic attenuation coefficient of the sample for the exciting wavelength.

A thick specimen can so be defined as one for which

$$\frac{I_h}{I_\infty} > 0.999 \quad \text{or} \quad k > 6.91 \quad (2)$$

For sufficiently small values of k , equation (1) can be approximated as:

$$\frac{I_h}{I_\infty} = k \quad (3)$$

Accordingly, a thin specimen can be defined as one with $k < 0.1$. Compared to equation (1), this relationship implies a relative error of 0.5% when $k = 0.01$, 1% when $k = 0.02$ and 5% when $k = 0.1$.

For specimens of intermediate thickness, only equation (1) is available. It is therefore necessary to develop correction methods, in order to take into account the effect of the thickness of the specimen on the intensity of the fluorescent radiation.

The emission-transmission method

Theoretical approach

By defining the transmittance T as the transmitted fraction of an X-ray beam through a material of thickness h and applying equation (1), we obtain:

$$T = 1 - \frac{I_h}{I_\infty} = \exp(-k) \quad (4)$$

By writing $k = -\ln T$ and as $k = \rho h \mu^*$ we obtain:

$$\mu^* = -\frac{\ln T}{\rho h} \quad (5)$$

$$\text{Thus } F(T) = -\frac{1-T}{\ln T} \quad (6)$$

$F(T)$ depends only on the specimen transmittance and integrates the absorption of the fluorescent radiation over the whole thickness of the specimen. It should be noted that $F(T)$ rapidly increases at small values of the transmittance and then progressively tends towards unity.

From the general equation of the fluorescence, we obtain:

$$I_h + G_i F(T) m_i \quad (7)$$

where G_i is a constant

The fluorescent intensity measured for a specimen of intermediate thickness is thus attenuated by the factor $F(T)$ owing to the absorption effect.

When T tends towards 1 (case of infinitely thin specimens), $F(T)$ tends towards 1 and equation (7) becomes:

$$I_h = G_i m_i \quad (8)$$

For intermediate thickness specimens, that is for $T < 0.9$, the intensity has to be corrected and the corrected intensity is defined by:

$$I'_h = \frac{I_h}{F(T)} = G_i m_i \quad (9)$$

The corrected intensity I'_h is consequently proportional to m_i . This relation is a remarkable generalisation of the fluorescence equation for a specimen of intermediate thickness.

Experimental determination of the transmittance

The procedure consists of the measurement of the X-ray absorption through the specimen, and the application of a corresponding correction to calculate the actual concentration C_i of the element i , component of the specimen. To measure the transmittance T , a radiator R containing a substantial concentration of the element i is used [3], as shown in figure 2.

The transmittance T of the specimen is given by:

$$T = (I_{R+s} - I_s)/I_R \quad (10)$$

Thus, to deduce the transmittance, three measurements are necessary:

- I_s , intensity of the specimen,
- I_{R+s} , intensity of the specimen with the radiator R behind,
- I_R , intensity of the radiator alone (maintained in the same geometrical position as for I_{R+s}).

Application to the correction of the fluorescent intensity

If the transmittance is higher than 0.9, the specimen can be considered as a thin layer, and the fluorescent intensity does not need correction. On the other hand, if the transmittance is lower than 0.9, the specimen is considered to be of intermediate thickness and the absorption effect has to be taken into account.

From equation (10): $I_{s \text{ corrected}} = I_{s \text{ measured}}/F(T)$.

It must be noted that $F(T)$ integrates the absorption of the fluorescent radiation over the whole thickness of the specimen.

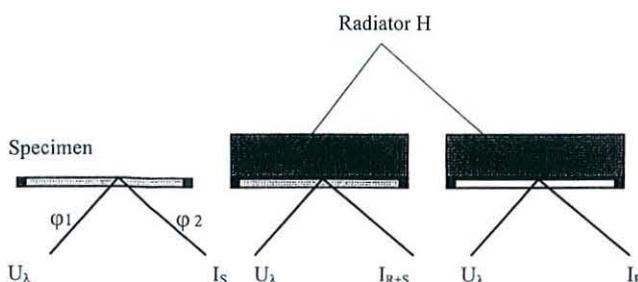


Fig 2. Emission-transmission method. The radiator technique (from [4]).

Experimental development

Selection of samples

The samples selected for this study were collected in Cape Verde Islands (16°45'N, 22°57'W), located in the Northern Tropical Atlantic (500 km from Dakar), by air filtration on polycarbonate filters (0.4 µm-pore-size Nuclepore®). The flow rate of air filtration ranges between 0.5 and 1 m³.h⁻¹, for a collect duration of 24 h, and thus the air volumes filtered range between 10 and 24 m³.

This aerosol is roughly composed of a mixture of terrigenous aerosol (associated with Saharan dust pulses) and sea salt, in variable proportion from one sample to another. The choice of elements to analyse by X-ray fluorescence includes soil (Si, Al, Fe and Ti), marine (Na, S) and mixed origin (K, Ca) 'traceurs'. It should be noted that sulphur may also constitute an important contribution from anthropogenic sources. Thus, the method of transmittance measurements has been applied for all these elements, except sodium for which transmittance measurements can not be made because the only blank filter already absorbs completely the signal from the Na 'radiator'.

The principal characteristic of this aerosol type is the large range of mass of matter collected on the filters. This is due to the great variability of Saharan dust pulses in this region. Thus, we selected about ten samples, at different loads of iron mass on filter; indeed this element emits the most energetic radiation, which is absorbed the least.

Choice of radiators

For some of the selected elements, such as iron, aluminium, silicon, we directly used bulk samples containing almost exclu-

Table I. Elemental concentrations in radiators used for the transmittance measurements.

	Fe	Al	Si	Ca	K	Ti	S
Bulk sample	> 90%	> 90%	> 99%				53%
Glass disk			5%	15%	9%	6%	4%

sively the element to be measured. On the other hand, for elements such as calcium, potassium and titanium, it has been necessary to make glass disks containing a high concentration of the measured element, but diluted in a lithium tetraborate flux [5]. For sulphur, the transmittance measurements have been performed with a bulk sample of pyrite (FeS₂). The different radiators available for this study are presented in table I.

The main problem when using different kinds of radiators (bulk samples and glass disks) concerns the possible influence of the elemental concentration in the radiator on the transmittance measurement, particularly for measurements performed on high loaded samples. Thus, we operated transmittance measurements for Si and S by using two radiators with quite different elemental concentrations. For sulphur, the transmission measurements have been performed with the disk glass containing 4% of S (potassium sulphur diluted at 20%), and compared to those made with the pyrite (53% of S). For the silicon, we operated in the same way, a first measurement with the glass disk containing 5% of Si (silicon dioxide diluted at 10%), and a second with a pure metal sample (metallic silicon).

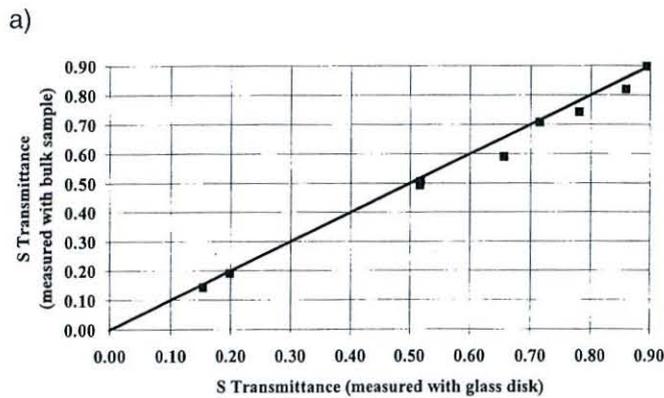
The results are presented in figure 3a and b. They show a good agreement, according to experimental uncertainties, for the two tested elements. The mean discrepancy between the two measurements is lower than 5%. Thus, we can conclude that the elemental concentration in radiator, for this study, has little influence on the transmittance measurement.

Results

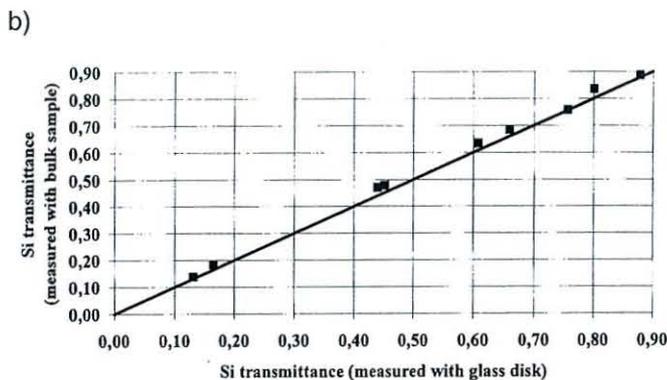
Table II presents, for each element, the measured transmittance as a function of iron mass (without correction) in the sample in agreement with the direct thin layer method [1] by directly using equation (8). It should be noted that the iron is indeed the element for which the absorption effect is the weakest. We also observe that the absorption effect increases from heavy to light elements, aluminium presenting the most important absorption effect among the analysed elements. Finally, the results show that the transmittance values ranged between 0.99 and 0.11. The most important fact is that many samples have to be considered to be of intermediate thickness, and consequently absorption corrections are necessary.

Table II. Transmissions measured with the radiator technique as a function of iron mass (µg/filter).

N° Sample	m _{Fe} (µg/filter) non corrected	T (Fe)	T (Ti)	T (Ca)	T (K)	T (S)	T (Si)	T (Al)
1	2		0.994		0.990	0.985	0.980	
2	6			0.957				
3	12		0.960		0.921	0.820	0.836	0.791
4	12							0.809
5	20	0.990	0.975	0.957	0.949	0.897	0.888	0.893
6	40		0.941		0.897	0.742	0.758	0.736
7	56		0.929		0.879	0.707	0.685	
8	78	0.965	0.919	0.868	0.852	0.589	0.634	0.609
9	92		0.839	0.772	0.73	0.493	0.471	0.405
10	123	0.945	0.864	0.802	0.768	0.505	0.479	0.427
11	148							0.387
12	245	0.888	0.741	0.639				0.194
13	298	0.832	0.647	0.528	0.474			0.125
14	376	0.833	0.637	0.507	0.440	0.143	0.138	0.115
15	393	0.825						
16	448	0.820						



Mean discrepancy between the 2 measurements series: 4.23%



Mean discrepancy between the 2 measurements series : 4.71 %

Fig 3. Comparison of transmittance measurements with two different radiators (glass disk and bulk sample) and mean discrepancy between the two measurements for a) sulfur and b) silicon.

Correction methods

Direct corrections - estimations

For samples whose transmittance is lower than 0.9, it becomes possible to correct the measured intensity and consequently the concentration because the correction factor $F(T)$ only depends on the transmittance. It must be noted that, due to the use of elemental radiators, these measurements have to be performed sample by sample, but also element by element, which can be a little long and tedious. Therefore, we decided to look for a relation between the aerosol mass and the absorption. Indeed, the absorption coefficient is related to the mass per unit area ($\text{g}\cdot\text{cm}^{-2}$) of the sample by:

$$k = \rho h \mu^* = m \mu^*$$

with μ^* depending on the absorption (of both incident and fluorescent radiation) by the sample matrix.

First, we chose the transmittance measurements performed on iron, the analysed element whose radiation is the least affected by the absorption effect; we observed a linear relation between the iron mass on the filter (μg) and the absorption coefficient k measured, with a correlation coefficient value of 0.98 (fig 4). This means that a constant μ^* , or a fixed composition matrix, allows the assessment of the iron absorption. Then, we calculated the corrected concentrations from this linear regression, and compared the values obtained with the

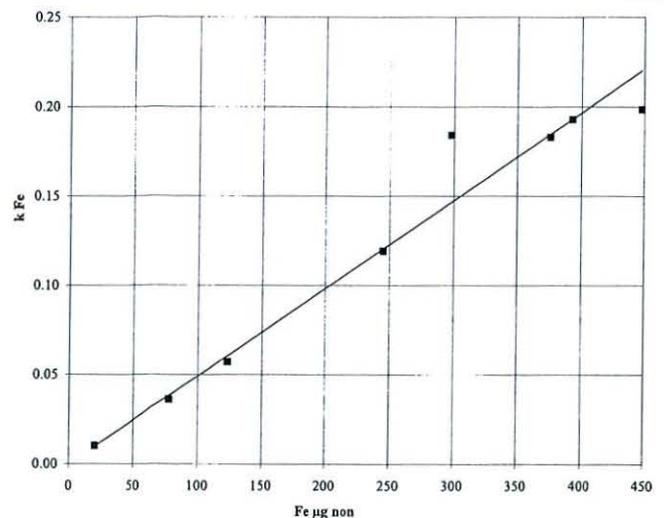


Fig 4. k measurements as a function of Fe mass on the filter (non-corrected) and correlation coefficient associated with iron.

concentrations directly corrected by the transmittance measurements. The results are presented in table III. It must be noted that the mean error on the corrected concentration of iron is 0.81%; so, this result indicates that it is possible to correct in this way (interpolation with the linear regression), with a good confidence, the iron concentrations even for samples for which the transmittance has not been measured.

We tried to apply this procedure to measured transmittances for the other elements, by defining linear regressions of absorption coefficients as a function of the corrected mass of iron. Figure 5a-f presents the results obtained, respectively, for titanium, calcium, potassium, sulphur, silicon and aluminium. The respective correlation coefficients r , and mean errors between the directly corrected concentrations (determined by the measurements) and those using the regression are presented. We note that, for the whole measurements, the correlation coefficients values are at least 0.97. The mean error on the corrected concentrations varies from 1.01% for titanium to 5.17% for aluminium; we observe, indeed, an increasing error on the corrected concentrations, with increasing absorption, the correction on concentration being more important. But in all cases, the errors are limited, since they are at the most around 5%, which is a classic error margin for thin layer analysis by X-ray fluorescence.

Table III. Comparison between iron mass corrected directly by transmittance measurements and by linear regression; discrepancy between the two calculations.

m_{Fe} ($\mu\text{g}/\text{filter}$) non corrected	m_{Fe} ($\mu\text{g}/\text{filter}$) after correction by T measured	m_{Fe} ($\mu\text{g}/\text{filter}$) after correction by the regression	Discrepancy
20	20.1	19.6	2.25%
78	79.4	79.3	0.08%
123	127	126	0.04%
245	260	260	0.12%
298	326	321	1.69%
376	411	413	0.50%
393	432	434	0.46%
448	494	501	1.35%
			0.81%

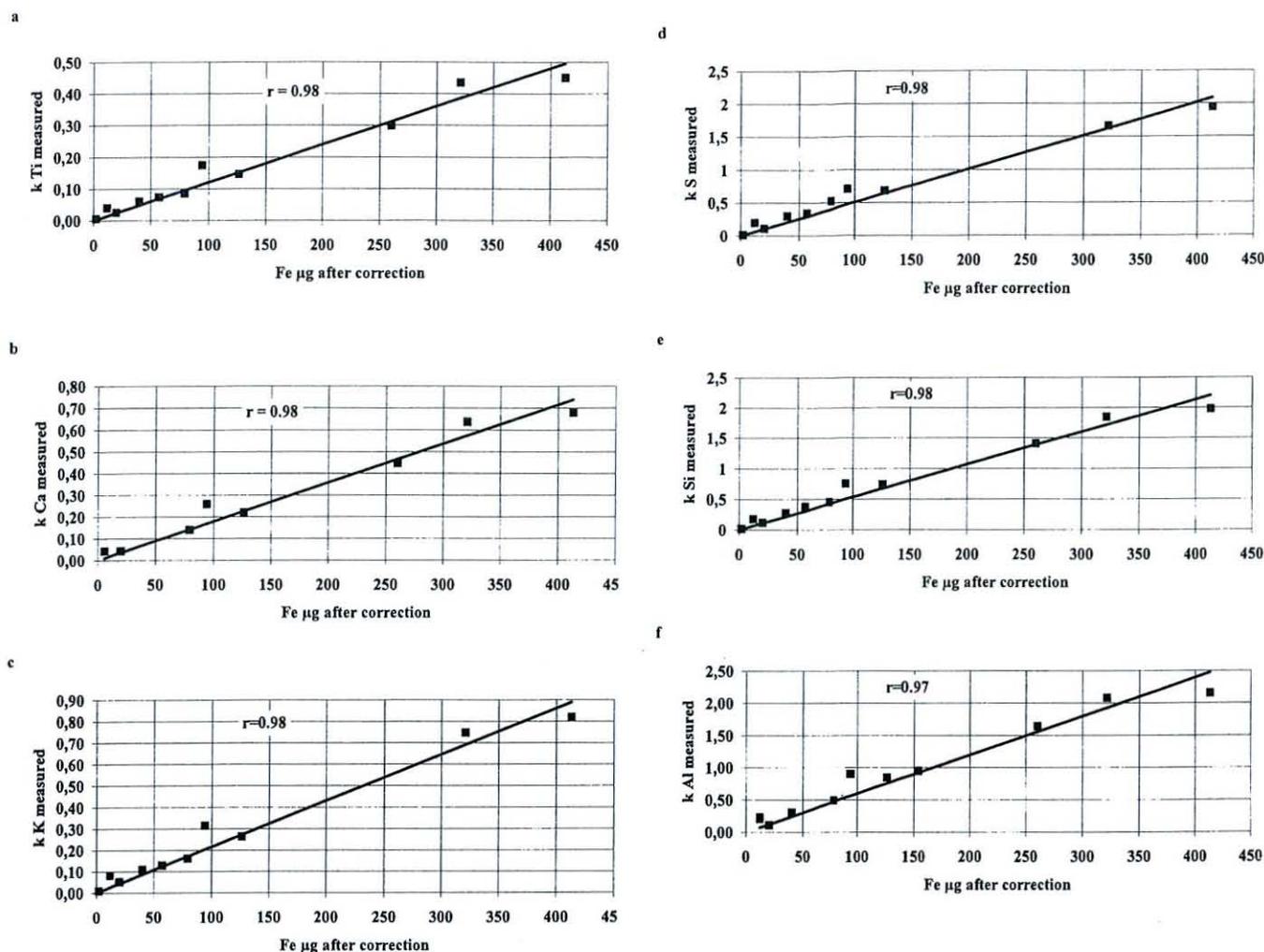


Fig 5. k measurements as a function of Fe mass (after correction) and correlation coefficients associated with a) titanium, b) calcium, c) potassium, d) sulfur, e) silicon and f) aluminium. Mean error on the corrected concentration using regression for the calculation.

Therefore, with these linear regressions, it has been possible not only to correct the concentrations for each measured element over the whole set of samples collected in Cape Verde Island, but also to determine easily the limits of thin layer analysis which, obviously, are only available for this aerosol type, which is a specific mixed composition with Saharan dust and marine aerosols.

Table IV summarises the iron corrected mass values (μg), beyond which the thin layer hypothesis is not valid (that is for which $k_i = 0.1$), for each analysed element.

It appears, obviously, that the analysis of lighter elements will determine the limit to adopt; the maximum mass of iron to correctly analyse aluminium as thin layer is $17 \mu\text{g}$ by filter; beyond this value, corrections have to be made for aluminium analysis. By contrast, for the other elements, the limit values are superior, eg for iron (which emits the most energetic radiation), which can be analysed without correction up to $224 \mu\text{g}$ by filter.

Table IV. Thin layer analysis limits determined from linear regression of transmission measurements as a function of iron mass ($\mu\text{g}/\text{filter}$) after correction, for the case of Cape Verde Island aerosols.

Analysed element	Fe	Ti	Ca	K	S	Si	Al
m_{Fe} ($\mu\text{g}/\text{filter}$) limit	224	83	56	46	20	19	17

The limits of thin layer analysis could be expressed as a function of the total mass of matter on filter, or of the sample thickness, if the matrix composition was known.

As shown previously, for each analysed element, the absorption is a linear function of the iron mass on filter. It means that a matrix should exist of a given composition that allows the representation of absorption measurements performed for this set of samples. Thus, it could be particularly interesting to determine this matrix composition.

Development of an absorption model

The purpose is to reproduce by calculation the absorption coefficients previously measured, from a matrix whose composition has to be determined.

For that, the definition of the absorption coefficient has been used:

$$k = \rho h \mu^* = m \mu^*$$

$$\text{with } \mu^* = \frac{\mu_{s,\lambda e}}{\sin \psi_1} + \frac{\mu_{s,\lambda i}}{\sin \psi_2} \quad (m \text{ is in } \text{g}\cdot\text{cm}^{-2} \text{ and } \mu^* \text{ in } \text{cm}^2\cdot\text{g}^{-1})$$

The calculation of μ^* is possible since the mass absorption coefficients of the matrix are additional in relation to mass absorption coefficients of elements contained in the matrix. Thus, if $\mu_{j,\lambda i}$ represents the absorption of element j at the wavelength of the fluorescent radiation of element i , and x_j the relative concentration of element j in the matrix, so:

$$\mu_{s,\lambda_i} = \sum_j \mu_{j,\lambda_i} \chi_j$$

Thus, since the mass absorption coefficients for elements are available in tables [6], it is possible to calculate, for a given elemental composition of matrix, the absorption of elements at wavelengths of excitation and fluorescent radiations used for the measurements. This calculation has been performed using the specific X-ray calculation software 'ProFX'[7]. The total mass of the matrix is calculated from an element of well-known concentration in the matrix, iron being obviously the best adapted one, considering the previous results.

This calculation has been made with two major constraints. First, to reproduce as well as possible the absorption coefficients measured. To do this, we choose to minimise the deviations for three major elements whose absorptions are very different: iron (the least absorbed), calcium (of intermediate absorption) and aluminium (the most absorbed). Thus, the other elements are used as tests, in order to verify that the adopted matrix also reproduces correctly their absorption. Second, it is clear that the matrix must have a realistic composition with regard to the aerosol kind collected on filters. This means that the matrix must have a composition as close as possible to a mixture of terrigenous aerosol and sea salt.

Table V presents the matrix composition obtained, in agreement with these two constraints. The elemental concentrations of this matrix are very close to those of a mixture of 75% of terrigenous aerosol and 25% sea salt, in comparison with crust [8] and sea water [9] models usually used in geochemistry.

The deviations between absorption coefficients measured (linear regressions) and calculated from this matrix are presented in figure 6a–g, respectively, for iron, calcium, aluminium (solved), titanium, potassium, sulphur and silicon (tested). The error introduced by the calculation is also presented, the maximum error being observed for aluminium, for which the calculation overestimates the absorption of 11%. However, the error on calcium K_{α} absorption is weaker with a value around 6% and the iron K_{α} absorption calculated with the matrix is in a perfect agreement with the measurements. This is particularly important since the calculation of the total mass of matter will be made from this element concentration.

Concerning the 'test' elements, even if the error for silicon K_{α} absorption calculation remains rather important (around 10%), we observe good agreements for the other elements with error values lower than 4%.

This result is particularly important since it means that from this matrix, and for this set of samples, one can estimate the absorption coefficients for other elements for which absorption has not been measured. For example, it is possible to calculate the absorption on the K_{α} sodium radiation, which is assessed to be particularly important, by this matrix with an estimated error lower than 20%. The linear regression obtained is presented in figure 7.

Table V. Elemental composition of the matrix adopted for absorption calculation.

Element	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Mn	Fe
Relative concentration (%)	25	5	0	7.8	20	5	20	3	7.2	0	0	7

Table VI. Thin layer analysis limits deduced from the absorption calculation as a function of iron mass ($\mu\text{g}/\text{filter}$), total mass ($\mu\text{g}/\text{filter}$) and sample thickness (μm).

Element	Fe	Ti	Ca	K	S	Si	Al	Na
Fe mass ($\mu\text{g}/\text{filter}$)	224	87	60	48	20	17	15	8
Total mass ($\mu\text{g}/\text{filter}$)	3200	1243	857	686	286	243	214	114
Sample thickness (μm)	2.25	0.87	0.60	0.48	0.20	0.17	0.15	0.08

It is also interesting to calculate the thin layer analysis limits for this kind of matrix, element by element. Table VI presents the results obtained as a function of the iron mass, also of the total mass of matter of the sample and of the sample thickness (calculated considering an aerosol density of $2.5 \text{ g}\cdot\text{cm}^{-3}$). It must be noted that these thin layer analysis limits are in very good agreement with those previously obtained experimentally (see table IV). Consequently they can be calculated for other elements (such as Na) with a good confidence.

Conclusion

The emission-transmission method developed by Leroux and Mahmud [3] has been applied to a set of atmospheric aerosol samples of mixed origin (terrigenous and marine) collected in Cape Verde Island. Transmittance measurements performed for seven elements (Al, Si, S, K, Ca, Ti and Fe) have allowed the determination of the thin layer analysis limits for this type of aerosol, and the correction of concentrations for the cases presenting an absorption effect.

We note that, for the analysed elements, many samples must be considered to be of intermediate thickness, and that the concentration corrections associated with the absorption effect were particularly important. Furthermore, the measurements performed for about ten samples selected at different loads of matter allow the correction of concentrations for the whole set of samples, a linear relationship being found between the mass of matter on the filter and the absorption, with differences lower than 5%.

Therefore, a theoretical absorption model, adapted to this set of samples has been developed in agreement with experimental results. A matrix of composition close to that of a mixture of 75% of terrigenous aerosol and 25% of sea salt allows us to reproduce correctly the absorption effects. In this way the estimation of the absorption for elements for which the transmittance measurements have not been performed, such as sodium, is possible with an error estimated lower than 20%. The limits of thin layer analysis calculated in this way are in good agreement with those previously deduced from transmittance measurements.

The procedure proposed here seems to be particularly interesting since it does not necessitate the previous knowledge of the matrix (in contrast, it allows the determination of the matrix composition) and therefore can be applied to other aerosol types.

Nevertheless, only the absorption effect by the matrix has been taken into account for this study, although an absorption effect by the particle size itself is also possible, particularly for light elements, such as sodium. To take into account this effect, a comparison with another analytical method (such as atomic absorption) would be necessary. But to check the perfect validity of the transmission-absorption method, we must unfortunately use techniques such as AAS or AES-ICP that destroy the

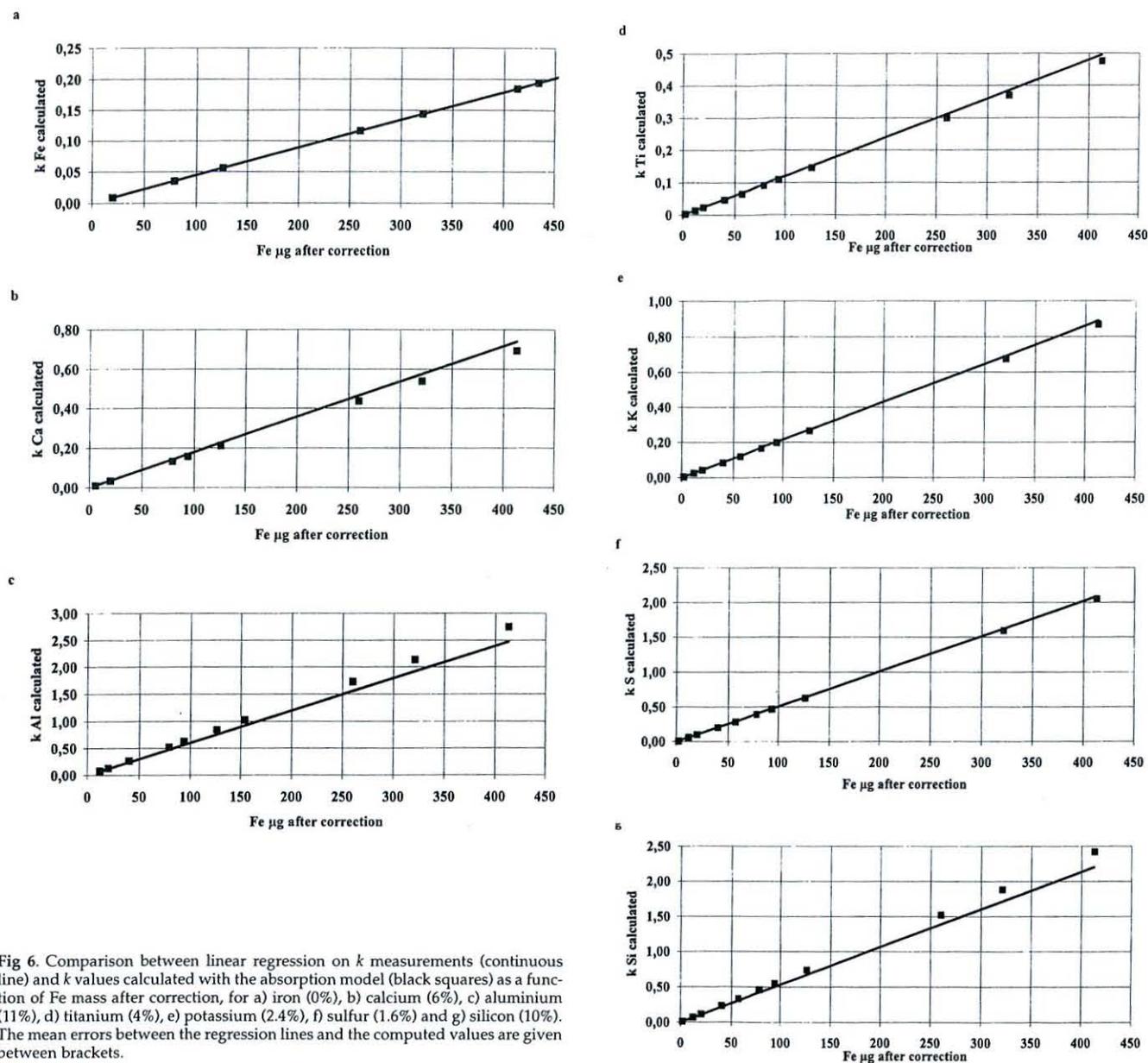


Fig 6. Comparison between linear regression on k measurements (continuous line) and k values calculated with the absorption model (black squares) as a function of Fe mass after correction, for a) iron (0%), b) calcium (6%), c) aluminium (11%), d) titanium (4%), e) potassium (2.4%), f) sulfur (1.6%) and g) silicon (10%). The mean errors between the regression lines and the computed values are given between brackets.

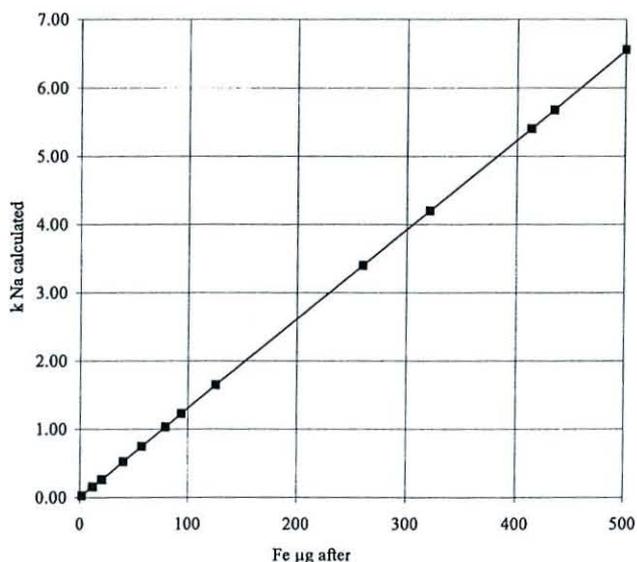


Fig 7. k values estimated from the calculation as a function of Fe mass (after correction) for sodium.

sample in order to have a homogeneous solution. Furthermore, all the elements of interest are not solubilised in the same kind of digestion solution: acidic for metals and basic for silica, for example. The solution to this problem may be found by performing the transmission-absorption method on filters with standard materials deposited by filtration.

References

- 1 Losno R, Bergametti G, Mouvier G, *Environm Technol Lett*, 1987, 8, 77-86
- 2 Aloupogiannis P, *Analisis*, 1987, 15, 347-354
- 3 Leroux J, Mahmud M, *Anal Chem*, 1966, 38, 76-82
- 4 Tertian R, Claisse F, *Principles of Quantitative X-Ray Fluorescence Analysis*, Heyden London, 1982
- 5 Quisefit JP, de Chateaubourg P, Garivait S, Steiner E, *X-Ray Spectrometry*, 1994, 23, 59-64
- 6 Leroux J, Think TP, *Tables révisées des coefficients d'absorption masique des rayons X*, Claisse Scientific Corporation, Québec, 1977
- 7 Steiner E, *Analisis*, 1991, 19, 29-30
- 8 Mason B, *Principles of geochemistry*, J Wiley and sons ed, 3rd edition, New York, 1966
- 9 Brewer P, In: *Chemical Oceanography* (Riley JP, Skirrow G eds), 2nd ed, vol 1, Academic, New York, 1975, 415-496