

## COMPARISON BETWEEN THIN-FILM XRF AND ICP-OES FOR THE ANALYSIS OF SUSPENDED PARTICULATE MATTER

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### ABSTRACT

Suspended matter samples from the NW German waddensea and from two NW German rivers were analyzed by thin-film X-ray fluorescence analysis (XRF) and by inductively coupled plasma - optical emission spectrometry (ICP-OES) for Si (only XRF), Ti, Al, Fe, Mg, Ca, Na, K, and Mn. Calibration for thin-film XRF was carried out using ultra-fine grained rock powders which were suspended in water and brought onto membrane filters by vacuum-filtration. It is shown that the particle size correction calculations known from literature are not practicable for this application. The comparisons between the results of thin-film XRF and ICP-OES demonstrate, that the deviations were large for the light elements, which is explained by particle size effects in the case of the coastal marine samples and by matrix effects in the case of the relatively iron-rich river samples. Application of thin-film XRF can be recommended for the analysis of Fe and Mn. For these two elements thin-film XRF is a quick, reliable and additionally a non-destructive method for very small sample amounts in the range of 1 to 4 milligrams. The combination of membrane filtration, acid digestion and simultaneous ICP-OES is recommended when sample amounts are higher, time is less important, and more elements, including trace elements, are to be measured. For the determination of the element Si the described thin-film method is considered as a half-quantitative method.

### INTRODUCTION

Thin-film x-ray fluorescence has been described as a useful method for the analysis of major elements in different kinds of samples. In the 1950's to 70's it has for example been applied for thin metal- or oxide-films (Liebhafsky, 1954; Rhodin 1955), films of paint (McGinnes et al., 1969), and precipitated metal compounds (Luke, 1968; Panayappan et al., 1978). More recent applications are those on environmental samples like aerosols (Gilfrich et al., 1973; Eberspächer & Schreiber, 1976; Dzubay, 1977; Quisefit et al., 1994) or particulate matter from the aquatic environment (Cann & Winter, 1971; Baker & Piper, 1975; Vanderstappen & Van Grieken, 1976).

Most interesting for the use of a thin-film method is not a low limit of detection, but the possibility to investigate very small sample amounts, in the range of a few milligrams. Another advantage is, that only very little sample preparation is required, in this work only filtering, drying and weighting before the measurement of suspended matter.

Nevertheless, attention has to be paid for environmental particulate matter, because of the particle size effects, which have already been described in detail elsewhere (Claisse & Samson, 1962; Lubecki et al., 1968; Berry et al., 1969).

Inductively coupled plasma - optical emission spectrometry (ICP-OES) is known to be a reliable method for the analysis of major and minor elements in a wide variety of geological samples (e.g. Heinrichs and Herrmann, 1990). For simultaneous ICP-OES the amount of sample needed is low compared to the classical methods like gravimetric, titrimetric, or photometric methods, flame emission or flame atomic absorption spectrometry. Therefore it is also suitable for the analysis of suspended matter from the aquatic environment.

In this paper we first discuss the application of particle size correction calculations for thin-film XRF. Particle size effects of our thin-film XRF method that is similar to the method described by Baker and Piper (1976) are demonstrated by the measurement of geostandards. The critical filter loading mass for thin-film XRF is evaluated and calibration is performed using four international geostandards with different filter loading masses respectively. The application of the thin-film method for the analysis of major and minor elements in natural suspended matter from the NW German waddensea and NW German rivers is tested by a comparison to the results of acid digestions measured by ICP-OES.

## THEORY OF THIN-FILM XRF

Thin-film x-ray fluorescence deals with samples which ideally are infinitely thin according to exciting radiation (primary) as well as characteristic (secondary) radiation. This means that the characteristic radiation generated in the sample is ideally not diminished.

In general the loss of intensity of the characteristic radiation of an element transmitting a sample of the thickness  $t$  can be described by the following expression:

$$dI = k \left( \frac{1}{\sin \phi} \right) I_0 \cdot e^{-\left\{ \left[ \left( \frac{\mu}{\rho} \right)_{\lambda, \text{pri}} \cdot \frac{1}{\sin \phi} + \left( \frac{\mu}{\rho} \right)_{\lambda, \text{L}} \cdot \frac{1}{\sin \psi} \right] \rho t \right\}} dt \quad , \text{Gunn (1967)}$$

(1)

where

$\rho$  = density of the sample in  $\text{g/cm}^3$

$\phi$  = angle between primary beam and sample surface

$\psi$  = angle between sample surface and secondary beam

$\lambda, \text{pri}, \lambda, \text{L}$  = wavelengths of primary- and analyte-line respectively

$(\mu/\rho)_\lambda$  = mass absorption coefficient of the sample at a wavelength  $\lambda$  in  $\text{cm}^2/\text{g}$

In case of a very thin sample the absorption of x-rays will be very small or approximately zero. So the exponential term of the foregoing equation will become negligible, resulting in

$$dI = k \frac{1}{\sin\phi} I_0 dt, \text{ or } \Delta I = k \frac{1}{\sin\phi} I_0 \Delta t. \quad (2)$$

For a constant sample area  $\hat{a}n$  ( $n$  = atom number of the analyte ) can be regarded as proportional to  $\hat{a}t$ .

$$\Delta I = k \frac{1}{\sin\phi} I_0 \Delta n \quad (3)$$

This means that in case of a thin sample film an increase in intensity  $I$  is linearly dependent on the absolute number of analyte atoms. If primary beam intensity and the angle  $\phi$  are kept constant, the expression simplifies to

$$\Delta I = k' \cdot \Delta n. \quad (4)$$

After Berry et al. (1969), Criss (1976), and Holmes (1981) it is necessary to carry out a particle size correction, when analyzing particulate matter.

Criss (1976) proposed that the loss in sensitivity, given by the relationship between  $s_0$  (sensitivity for the ideally thin-film) and  $s_i$  (measured real intensity) can be described by a factor which takes mean particle sizes ( $a$ ) as well as the composition of the particles and the experimental conditions (coefficient  $b$ ) into consideration.

$$(1 + ba) = \frac{s_0}{s_i}, \text{ Criss (1976)} \quad (5)$$

With the correction method from Holmes (1981) it is taken care of the multimodal particle size distribution of natural particulate matter. As an expression for the degree to which observed or theoretically received signal approximates thin-film response he gives

$$\Gamma = X^{-1} \int_0^X I dx \quad (6)$$

with the film thickness  $X$  and the intensity  $I$ . For real sample measurement conditions the signal loss for a given element through the sample as a whole is described by

Holmes (1981) as

$$\Gamma_{\tau} = \sum_{i=1}^{\eta} (\omega_i \Gamma_i) = \frac{\sigma_r}{\sigma_{\tau}}, \quad (7)$$

where

$i$  represents an individual size fraction within the sample

$\eta$  = number of such size intervals

$\omega_i$  = fraction of the sample mass within size interval  $i$

$\Gamma_i$  = median  $\Gamma$ -factor within size interval  $i$

$\sigma_r$  = elemental signal received at the detector from the sample as a whole for a given element

$\sigma_{\tau}$  = corresponding signal which would represent true thin-film response.

Dealing with natural particulate matter, which are composed of a complex mixture of minerals and organic matter, the application of a particle size correction as described by Criss (1976) is inconvenient or hardly possible. In his approach he uses mean particle sizes and he only gives coefficient "b" values for very few natural minerals, but mainly synthetic compounds. This method has so far only been verified by application on single compound samples (Wagman et al. 1978). For the particle size correction method after Holmes (1978) detailed information about the particles, e.g. what sort of mineral particles in the sample belong to which size interval, is needed. This in most cases might exceed the extent of information one would like to get by the analysis.

Since a particle size correction is not practicable, the only way to evaluate whether a thin-film method provides acceptable results seems, to measure the same samples with another, different analytical method.

## EXPERIMENTAL

### Preparation of thin-film samples

Calibration standards for thin-film XRF measurements were prepared similar as described by Baker & Piper (1976) with international geological reference samples (DR-N, GSR-5, MAG 1, W 2). This was considered as the best method, because grain size character and mineralogical composition (matrix) of the standards were expected to be similar to the natural suspended matter, which should be investigated. For testing the influence of particle size effects two additional in-house standards, a shale and a greywacke, were used. The standards were ground in an agate mortar, dry-milled with a Retsch-micromill or milled in state of a isopropanol-suspension with the Retsch-micromill. The sample

powders were afterwards suspended in 18 M $\Omega$  pure water and then sedimentated by vacuum filtration with a Satorius<sup>®</sup> polycarbonate filter system onto preweighted 0.4  $\mu$ m Nuclepore<sup>®</sup>-polycarbonate membrane filter. After filtration which lead to an even distribution of sample powder over the filter area, the filters were dried at 60 °C and weighted again to receive the sample mass.

Natural sea- and river-water suspensions were filtered and dried in the same way mentioned above. The waddensea samples which were taken in the Spiekeroog-island backbarrier tidal area (NW Germany) were prefiltrated through a 300  $\mu$ m sieve before filtration. After filtration the residue was rinsed with 10-20 ml 18 M $\Omega$  pure water to remove the sea salts. The river samples were taken from the Weser, south of Bremen (in Achim), and from the Hunte, in Oldenburg-Drielake and south of Oldenburg (in Dötlingen, Huntlosen, and Tungen). In contrast to the marine waddensea samples the filters were not rinsed after filtration.

All sample coated filters were stored in polycarbonate Petri dishes.

### **XRF instrumentation and measurement**

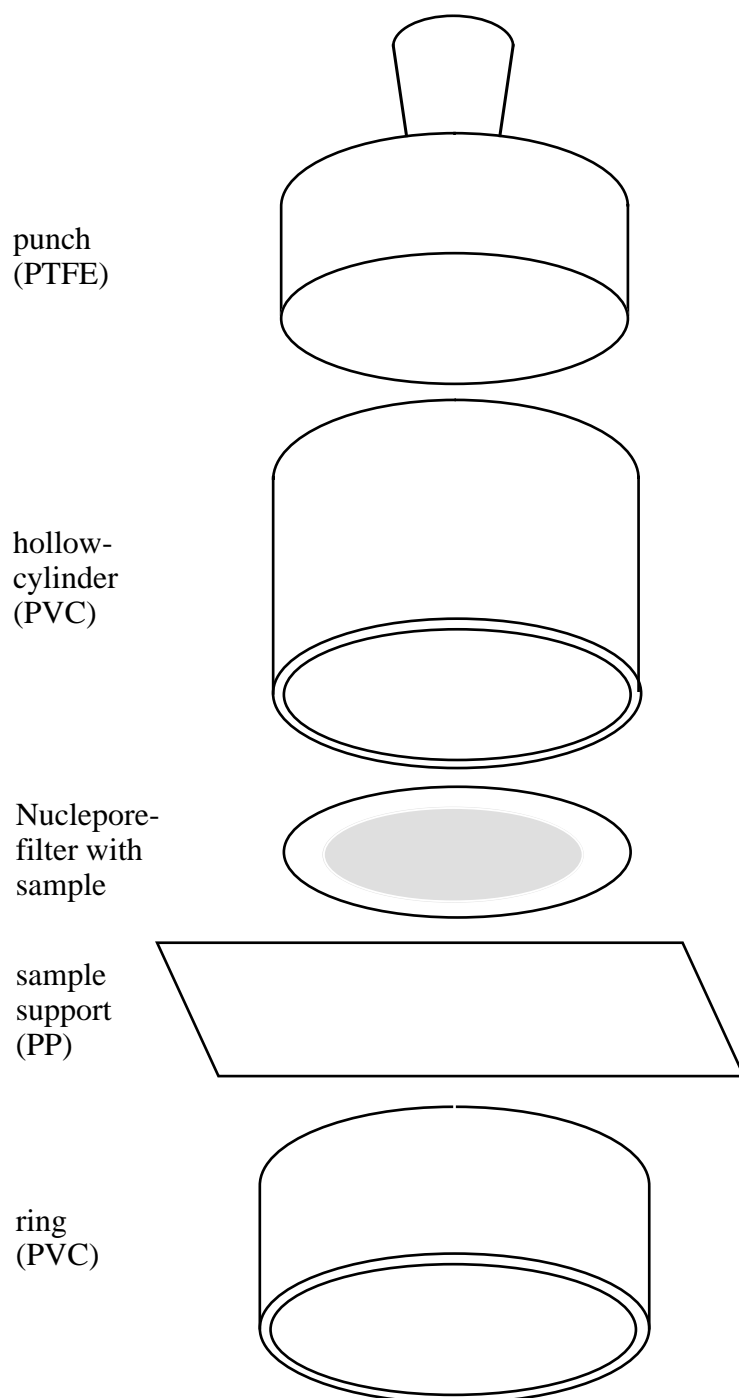
For measurement the sample coated filters were carefully fixed with Somar<sup>®</sup> polypropylene sample support onto the sample holder as shown in Figure 1. The size of the sample holder, an own-manufactured prototype, fits exactly with the sample cups of the spectrometer. A sample mask of 37 cm diameter has been used. The instrumental configuration of the Philips<sup>®</sup> PW 2400 sequential wavelength-dispersive X-ray spectrometer used for the measurements is shown in Table 1.

Precision of the method has been tested by replicate measurements of filter samples (precision of measurement), RSD-values (relative standard deviation) are included in Table 1.

### **Acid digestion of the filter samples**

For the ICP-OES measurements the following digestion method was applied.

Nuclepore filters with sample loadings between 5 and 10 mg were folded and put into a PTFE-vessel. 1.5 ml perchloric acid and 0.5 ml nitric acid were added, the vessels were closed and left for prereaction of the filter material over night (ca. 10 hours). Then the vessels were heated to 160 °C until the polycarbonate filters were completely destroyed (~ 4-5 h). After adding 0.5 ml perchloric acid and 1 ml hydrofluoric acid the vessels were closed for autoclave-digestion. They were heated within 5 h from 50 to 180 °C and left at this temperature for 5 h. After cooling the acids were fumed off on a hot plate (160 °C) until nearly dryness. 0.2 ml halfconcentrated hydrochloric acid was added and fumed off. The last step was done twice to obtain soluble chlorides of Al and Fe. The residue



**Figure 1.** Scheme of the thin film sample holder.

was then taken up with 0.5 ml nitric acid and brought to a volume of 25 ml.

### ICP-OES measurements

Simultaneous ICP-OES with a Perkin Elmer<sup>®</sup> Optima 3000 XL was taken as the reference method because it is fast and sample consumption is low. The optical emission lines and instrumental operating conditions we used are shown in Table 2. Precision of the measurement has been determined by replicate analysis (see Table 3). Accuracy of the

**Table 1.** Instrument parameters of the XRF-spectrometer and relative standard deviation of the measurements.

element	charact. line	kV	mA	crystal	collim. spacings	detector*	RSD (%)
Si	K $\alpha$	30	100	PE	0,7	FL	4,1
Al	K $\alpha$	30	100	PE	0,7	FL	5,0
Ti	K $\alpha$	40	75	LiF200	0,3	DU	3,4
Fe	K $\alpha$	60	50	LiF200	0,15	DU	2,3
Mg	K $\alpha$	30	100	TIAP	0,7	FL	5,8
Ca	K $\alpha$	40	75	LiF200	0,7	FL	3,9
K	K $\alpha$	30	100	LiF200	0,7	FL	5,5
Mn	K $\alpha$	50	60	LiF200	0,3	DU	3,2

\*FL: flow counter; DU: duplex= flow counter and sealed Xe-counter; SC: scintillation counter

whole method, including digestion, has been checked by measuring geostandards. A comparison with certified values is also given in Table 3.

## RESULTS AND DISCUSSION

### Particle size effects

The results for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> of three geostandards prepared by three different grinding procedures are shown in Figure 2 a-c. By measuring calibration curves of thin-film standards with different grain sizes and grain size distributions, particle size effects become visible. The in-house standards (shale and greywacke) which were only grinded for 20 minutes in an agate mortar and have a maximum grain size around

**Table 2.** Measurement conditions for ICP-OES analysis.

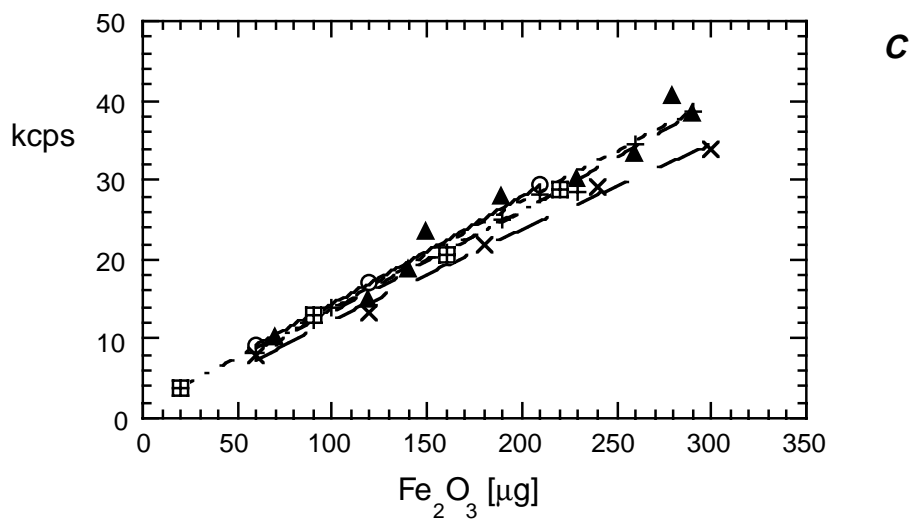
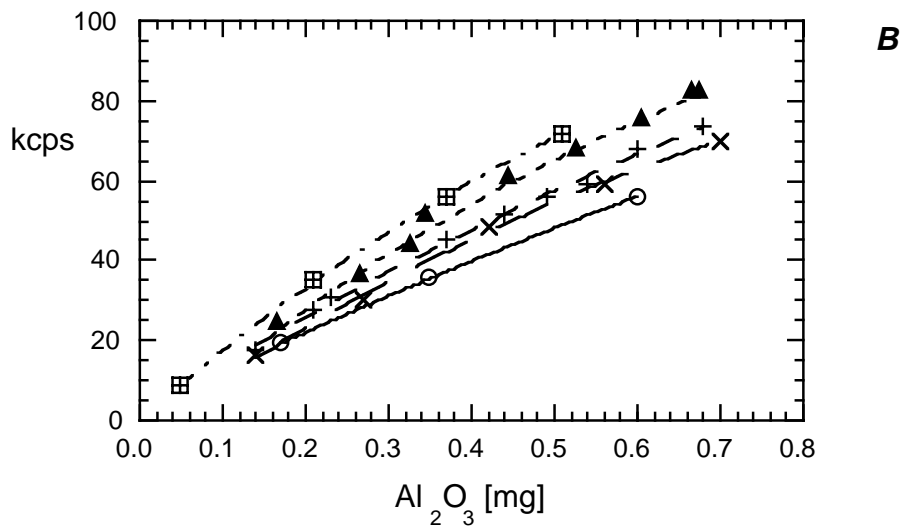
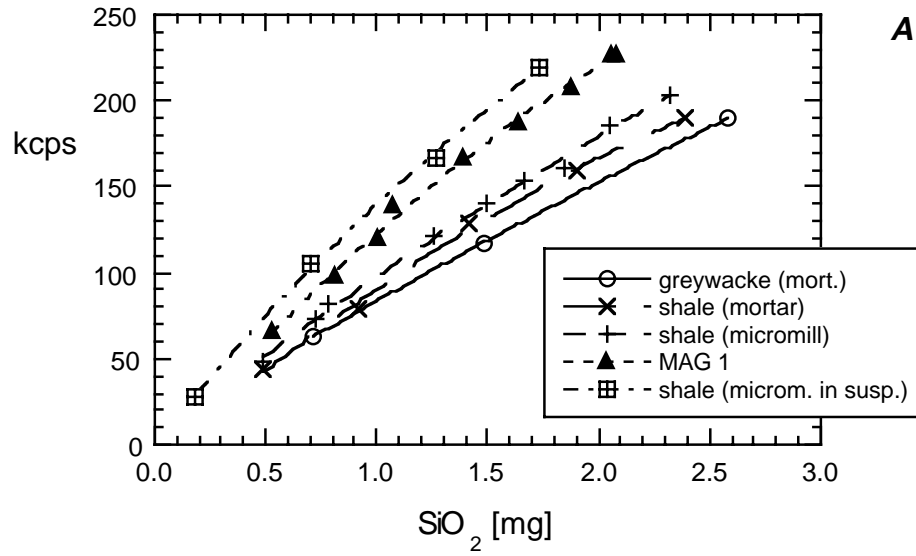
element	wavelength(s)	power (kW)	neb. flow (l/min)	calibration range
Al	308.215/309.271	1050	0.9	3-100 mg/l
Ti	334.941/336.121	1050	0.9	0.2-6 mg/l
Fe	238.204/259.940	1050	0.9	1-50 mg/l
Mg	279.079/279.553	1050	0.9	0.5-30 mg/l
Ca	317.933/422.673	1050	0.9	0.7-50 mg/l
K	766.490	1050	0.9	0.6-40 mg/l
Mn	257.610/260.569	1050	0.9	0.1-5 mg/l
nebulizer:		cross-flow		
main-gas flow:		15 l/min		
auxiliary-gas flow:		0.5 l/min		
plasma-view:		axial		

**Table 3.** Precision and accuracy of ICP-OES measurements; certified values of geostandards after Govindaraju (1994).

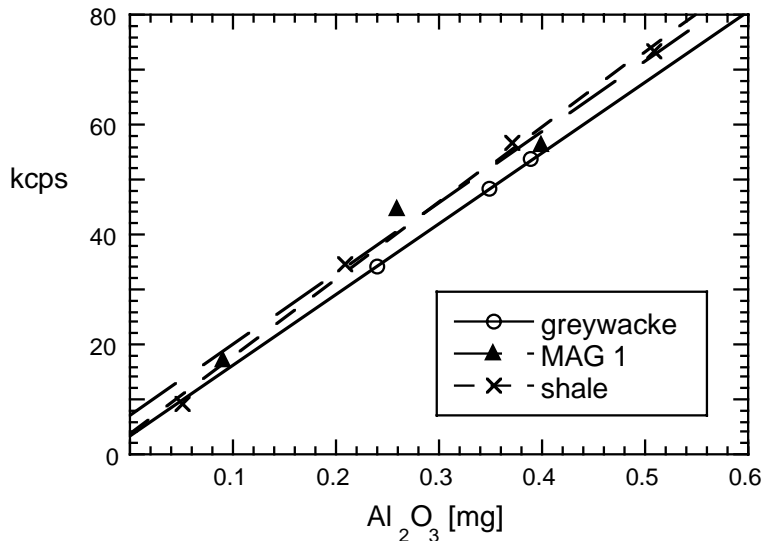
element	precision	accuracy					
		RSD (%)	DR-N		GSR-5		
			certif.	meas.	certif.	meas.	
Al	0,65	9,27	9,14	9,96	9,98	%	
Ti	0,48	0,653	0,645	0,396	0,406	%	
Fe	0,55	6,78	6,88	5,32	5,45	%	
Mg	0,62	2,65	2,54	1,21	1,19	%	
Ca	0,48	5,04	4,86	0,429	0,426	%	
K	0,62	1,41	1,53	3,45	3,34	%	
Mn	0,48	1704	1720	155	153	µg/g	

50 µm, show the lowest sensitivities (kcps per mg) for Si and Al. The shale sample which was grinded for one hour in a Retsch-micromill and has a maximum grain size of around 30 µm gives a calibration curve with a steeper slope. Finally, the sample, which was milled in the micromill for two hours suspended in isopropanol reaching a grain size maximum of 15 µm, shows the highest sensitivities, even higher than the MAG-1 (marine mud), which is already fine grained (30 µm grain size maximum). If the different samples, shale, greywacke and deep-sea clay (MAG-1) were all milled in suspension, they got very similar sensitivities, even for a light element like Al (see Figure 3). Heavier elements, like for example Fe, are not so drastically influenced by the particle size effects (Figure 2 c). The results for Si are influenced by the sample grinding procedure. This is possibly due to the fact that quartz (SiO<sub>2</sub>), which is a very common mineral in most rocks, is very resistant and though probably has large grain sizes in the standards. Although a preparation procedure for the calibration standards is found, a general problem is getting clear: Calibration samples and calibration curves can be optimized by a very long grinding procedure and thus by getting very fine grained standard-powders (see Figure 3), but not the natural particulates, which we intend to measure. Natural suspended matter from aquatic environments are very inhomogenous as well according to particle sizes as to the composition of the particles. They consist of a mixture of various mineral grains, organic matter and crustules of organisms, like for example diatoms. The size range of these natural particulates is very huge. For the suspended matter from the NW German waddensea we found particle sizes under a microscope of up to 50 µm for mineral grains and up to 200 µm for diatom crustules. The river samples showed much lesser particle sizes of up to 20 µm for minerals and up to 100 µm for organic debris.





**Figure 2.** Calibration functions of different samples.



**Figure 3.** Calibration lines of samples after the same preparation procedure.

### Critical filter-loading mass and calibration range

The critical filter-loading mass has been determined as the amount of standard sample powder on a filter (= area density in  $\mu\text{g}/\text{cm}^2$ ) up to which the sensitivity of detection (cps/ $\mu\text{g}$ ) of a given element is constant and no signal depression due to matrix effects occurs. For the elements Na, Mg, Al, and Si a value of  $175 \mu\text{g}/\text{cm}^2$ , for K and Ca  $220 \mu\text{g}/\text{cm}^2$  and for Fe, Ti, and Mn a value of  $275 \mu\text{g}/\text{cm}^2$  was received. This means that for example in thin-film samples with an area density over  $175 \mu\text{g}/\text{cm}^2$  the elements Na, Mg, Al, and Si cannot be measured properly, because they do not meet the thin-film criterion anymore. It must be pointed out that the above mentioned values are only valid for geological samples with a similar matrix than those used for calibration.

With a sample coated area of  $14.52 \text{ cm}^2$  of the filters, the absolute sample mass on the filters had to be in the range of 1.00, below which the weighting-error exceeded 1%, and 2.54 mg, to get all mentioned elements from Mg to Mn measured. The calibration-ranges and correlation coefficients of the calibration lines are presented in Table 4. Light elements have a characteristic radiation of low energy and thus are easily affected by particle effects as could be shown above (Figure 2 a+b and text). This is the reason why Si, Al, Mg and Na provided calibration-functions of relatively low quality.

### Evaluating the quality of the thin-film method

Suspended matter from eight different water samples from the NW German waddensea and five different water samples from rivers were analyzed by both methods, thin-film XRF and ICP-OES, for Ti, Al, Fe, Mg, Ca, Na, K, and Mn. Figure 4 illustrates how the results of the thin-film XRF measurements deviate from the results of the ICP-OES

**Table 4.** Calibration parameters of the thin film XRF method.

element	calibration-range	corr. coeff.
Si	550-1350 $\mu\text{g}$	0,9880
Ti	7-44 $\mu\text{g}$	0,9986
Al	162-430 $\mu\text{g}$	0,9815
Fe	80-346 $\mu\text{g}$	0,9964
Mg	37-104 $\mu\text{g}$	0,9863
Ca	20-340 $\mu\text{g}$	0,9991
K	12-103 $\mu\text{g}$	0,9962
Mn	1.2-6.9 $\mu\text{g}$	0,9985

measurements. For Al, Mg and Na the ICP-OES results are in most cases higher than the values measured by XRF. This is in agreement with the theory of grain size effects (Claisse & Samson, 1962; Lubecki et al., 1968; Berry et al., 1969) and can be explained by the particle sizes we found in the samples (see above). The characteristic radiation of the light elements is strongly effected by particle size and mineralogical effects. Consequently the heavier elements Ti, Ca and K were measured more accurate, but precision was still poor. Although the river samples do not have so large particle sizes, their thin-film XRF results do only agree with the ICP-OES results for the elements Fe and Mn. Since the river samples, especially those from the Hunte, show unexpectedly high contents of Fe and Mn, the problems seem to be caused by a matrix effect. Our calibration samples, common rock powders, have a lighter matrix than the river samples. Those may not meet the thin-film criterion with respect to the elements Na, Mg, Al, K, Ca, and Ti anymore. The waddensea samples do show deviations between the thin-film XRF and ICP-OES results for all measured elements including Fe and Mn. This is an effect of the larger grain sizes.

In summary the problems which became apparent for the thin-film method during the investigations lead to the conclusion, that this method cannot be recommended for clastic suspended matter from the coastal marine environment. If river suspended matter with small particle sizes (around 20  $\mu\text{m}$  Maximum) shall be measured, our thin-film XRF method can be used for the analysis of Fe and Mn. In this case thin-film XRF is a very quick and reliable method.

The ICP-OES-method described in this paper is a good alternative to measure suspended matter from a wide range of different aquatic systems, for a variety of major and minor elements. By simultaneous ICP-OES it is possible to measure several elements in one run, which makes it possible to analyze small sample amounts of 5-10 mg.

If Si shall be measured by ICP-OES, a special preparation of the samples is needed, which might be very time consuming. A half-quantitative determination of Si might in some cases be useful. We made the assumption, that Si behaves just like Al with respect

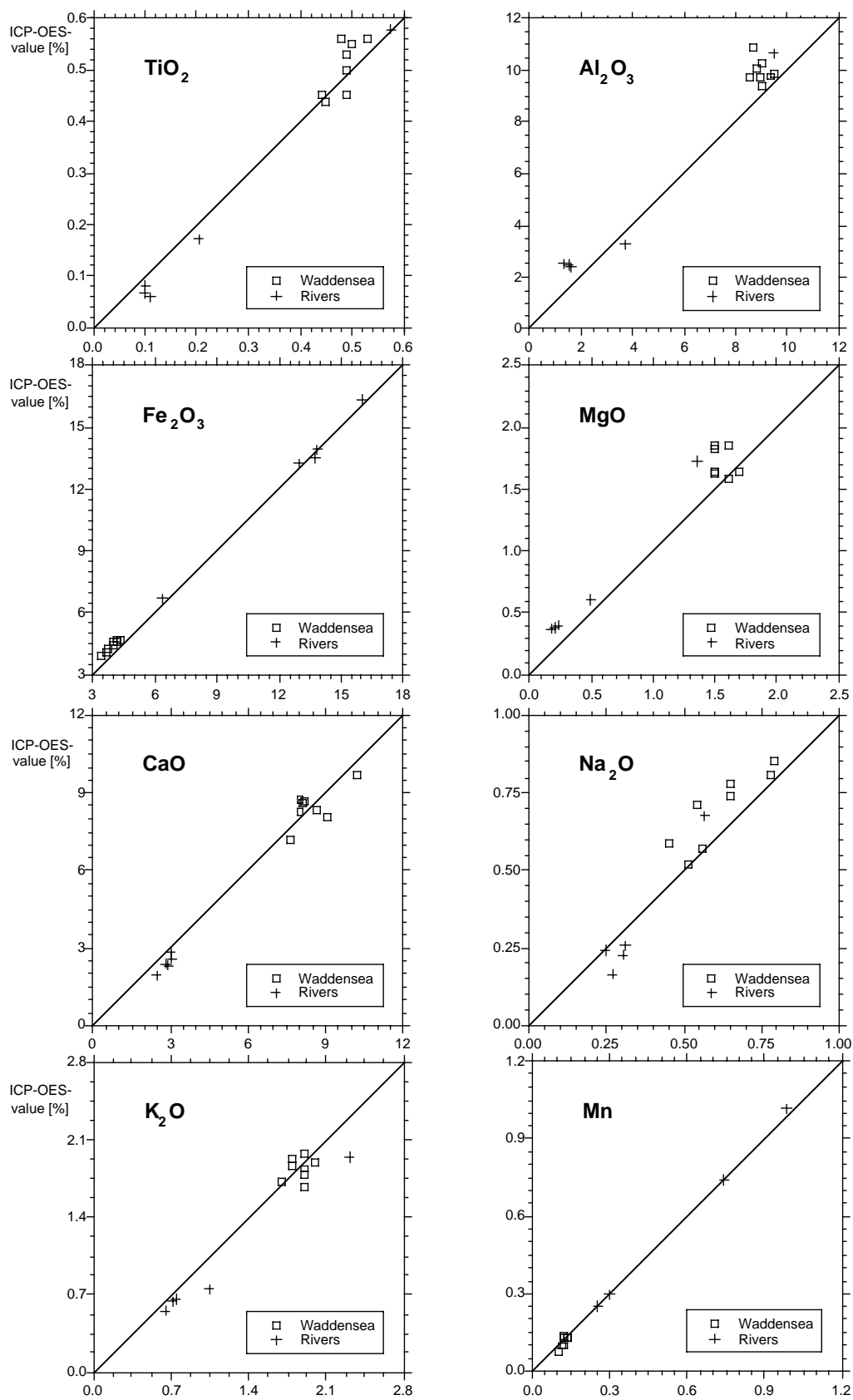


Figure 4. Comparison of ICP-OES and thin film XRF values.

to intensity loss during thin-film measurements. We calculated a mean correction factor of 1.2 for the samples from the waddensea and those river samples low in Fe (Weser) and a factor of 1.6 for the river samples with high Fe contents (Hunte). In the samples from the waddensea we could show an enrichment of quartz. In the river samples we were able to detect the occurrence or non-occurrence of diatoms by thin-film XRF.

## CONCLUSIONS

- Particle size correction calculations are not practicable in case of analyzing natural suspended matter from the water column by thin-film XRF.
- Comparisons between thin-film WD-XRF and ICP-OES measurements of natural suspended matter from a coastal marine environment as well as from rivers illustrated that
  - 1) the results of the XRF-method were too low for the light elements Al, Mg, and Na and the deviations are also too high for Ti, Ca, and K. Therefore thin-film XRF cannot be recommended for the analysis of these elements.
  - 2) the elements Fe and Mn can be measured in river suspended matter very accurate and precise by thin-film XRF, but not in suspended matter from the waddensea.
- In general an application of thin-film XRF on coastal marine samples cannot be recommended, because the material is too coarse grained.
- The combination of membrane filtration, acid digestion and simultaneous ICP-OES is a reliable method for major and minor element determination of suspended matter from coastal marine or other aquatic systems, like rivers.

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