ASSESSING THE ENVIRONMENT WITH X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT
In this paper we will introduce the general benefits of X-Ray Fluorescence spectrometry (XRF) for assessing the condition of the outer environment, especially where ambient aerosol particles are causing environmental disturbances. Examples from recent environmental studies are presented, and energy dispersive XRF is concluded to be a powerful, nondestructive yet easily applicable tool to supply detailed elemental information of particles collected in different applications. The further development and future potential of the method for detailed analysis of aerosol particles are discussed.

INTRODUCTION
Trace elements are essential for the environment and for human health, but at the same time inappropriate concentrations of the elements can cause considerable harm. To study the distribution of trace elements in the environment, to determine reasons for concentration changes and to estimate the possible consequences on the environment are challenging tasks for researchers of many research disciplines. The multi-element detection capacity, flexibility and low detection limits make the X-ray fluorescence technique (XRF) an excellent tool for the study of the elemental composition of environmental samples.

Many different X-ray fluorescence techniques can be utilized in environmental studies. They all share the benefits of being able to perform the analysis on trace levels in minute samples. In one end of the spectrum we have large scale facilities used to study small scale samples, i.e. synchrotrons around the world with beam lines devoted to micro-XRF studies. The Advanced Light Source team (ASL, 2005) in Berkeley, CA, USA lists over 40 synchrotron facilities worldwide. The synchrotrons with their high brilliance and collimated beams are well suited for analysis of samples where high spatial resolution is needed (Carvalho et al., 2007; Goldberg et al., 2007; Li et al., 2007), for image mapping of samples (Endo et al., 2008) and Total reflection X-Ray Fluorescence (TXRF) analysis of minute samples (Fittschen et al., 2008). At the Diamond
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facility in UK (Diamond, 2010), and at many others, a combination of µ-XRF, micro X-ray Absorption Spectroscopy (µXAS) and micro X-ray Diffraction (µXRD) opens up new possibilities to gain more information from the samples by combining different analytical techniques. Many authors have used the µXRF technique to study the spatial distribution of both toxic and essential elements in different materials. In many cases plants have been the focus of interest (Tian et al., 2010). At the other end of the spectrum, we have the small handheld spectrometers enabling XRF studies in the field, without the need to bring samples to a laboratory. The handheld instruments, or portable if we go up in dimension, are suitable for environmental investigations of for example contaminated land areas (Mielke et al., 2010) and deteriorated surfaces where the analysis can be linked to the influence on objects of art and cultural heritage (Kato et al., 2010; Nazaroff et al., 2010; Sianoudis et al., 2010).

The area on environmental applications of XRF is immense, and we will here focus on the analysis of the elemental composition of airborne particulate matter. Aerosol particles can be seen as a link between many of the other areas, since they may influence the environment on local, regional and global scales.

Particulate air pollution is a focus area of research and legislation in many parts of the world due to its effects on climate and air quality. For legislation and regulation purposes the particulate matter (PM) pollution is usually considered as a bulk parameter – the mass of the particles – without any further speciation of its content. XRF analysis of collected PM samples can help not only to understand the composition and its effects, but is also a valuable tool for source apportionment of the particles. This source apportionment can be done since there are known compositions of the most common sources and the size range in which they normally appear. This knowledge has been developing over a long time period and is based on circumstances from many different locations around the world. It is advantageous to have access to this knowledge but at the same time it must be treated with care since the local conditions may vary between different locations. The elemental composition obtained from traffic emissions are likely to differ between for example Gothenburg, Nairobi and Ouagadougou (Boman et al., 2009a; Boman et al., 2009b; Boman et al., 2010) due to their differences in infrastructure as well as vehicle fleet and fuel composition. This knowledge can give important clues for the abatement strategies used to tackle air pollution problems. This may be an especially efficient screening method in less studied areas like cities south of Sahara in Africa, which suffers from a multitude of problems that hinders a sustainable development.

Particulate matter is known to cause problems with both the human heart and the respiratory system at high concentrations. A connection between the increase in the concentration of fine particles (particles having an aerodynamic diameter of 2.5 µm or less - PM$_{2.5}$) and an increased mortality and hospitalization has been shown to exist (Dockery et al., 1993; Pope et al., 2002; Pope Iii et al., 2002; WHO, 2005; Chow et al., 2006; Pope et al., 2006; Pope et al., 2008). So far it is thought that small particles are causing the harm, with no lower size limit under which the
particles do not cause any harm. A recent paper by Perez et al. (Perez et al., 2008) on the other hand showed that there is a positive correlation between the mass concentration of Saharan dust particles with a size of 10 μm or smaller (PM$_{10}$) and mortality, while the same correlation was not found for PM$_{2.5}$. There is a need for a better understanding of the possible connection between the number and mass concentrations of particles, their content of organic and inorganic components and the causes of illnesses and hospitalization.

EXAMPLES OF XRF STUDIES OF PARTICLES

We here illustrate the potential of the XRF method for efficient and sensitive analysis of the PM in several urban environments from around the world. In the urban environment the analysis of the elemental composition of particles can be combined with knowledge about local and regional meteorology to determine possible sources or source regions of the different elements in the collected aerosol particles. In studies in Nairobi, Kenya and in Gothenburg, Sweden, (Boman, Gatari et al., 2009a; Boman, Petersson et al., 2010) local activities as well as long range transported (LRT) pollution were identified as contributors to the air quality of the cities. In Skopje, FYR of Macedonia, (Kovacevik et al., 2010) LRT particles were also identified, together with large contributions from local sources such as combustion processes, traffic and industrial activities. In studies by Molnar et al. (Molnar et al., 2005; Molnár et al., 2006; Molnar et al., 2007) links between the PM outdoors, indoors and possible health implications showed differences between the behavior of different elements, and in Beijing Sun et al. (Sun et al., 2009) looked at the composition of individual particles in the preparatory work before the Olympic Games in Beijing 2008. Results from these different studies are presented in further detail below.

Nairobi, source apportionment

In a recent study in Nairobi, Kenya (Boman, Petersson et al., 2010) PM$_{2.5}$ was collected at an urban background site approximately 1 km north (duplicate word) west of Nairobi city centre. Samples were collected on poly carbonate (PC) membrane filters using a plastic cyclone with the flow adjusted so that the size selective cut off was 2.5 micrometer. During week days the filters were exchanged daily while the changing time was increased to 48 hours between Saturday evening and Monday morning. In this way 100 samples were collected during the autumn and early winter 2008 with the aim to do apportionment of the sources of the collected particles.

The particle loaded PC filters were analyzed at University of Gothenburg, Sweden. The EDXRF spectrometer used is based on a setup with a secondary target to increase the signal to noise ratio though a three axial Cartesian geometry, figure 1. The X-rays from the Mo X-ray tube excite the Mo in the secondary target. The X-rays from the secondary target are used to excite the elements in the sample and a Silicon Drift Detector (SDD) is used to acquire the characteristic radiation of the elements and the scattered radiation from the secondary target. 50 kV tube voltage and 20 mA
tube current were applied, and for acquisition a livetime of 1800 s was used. The concentrations of black carbon and PM$_{2.5}$ were also determined on each filter.

![Figure 1](image_url)

*Figure 1. Schematic of the three axial Cartesian geometry of the EDXRF spectrometer.*

On average the determined concentrations of elements made up 6.2 % of the total PM$_{2.5}$ and black carbon was on average 22 % of the total mass. Cl, K, Ca and Fe had the highest concentrations, above 100 ng/m$^3$. The daily variations were large; the concentration of Fe for example varied from 8.4 to 1500 ng/m$^3$ between different days. These daily variations of elemental content as well as variations in BC and PM$_{2.5}$ concentrations were evaluated statistically in an attempt to identify sources that influence the particulate composition at the sampling site during the different days. The elemental composition of aerosol particles measured in Nairobi has been determined for more than a decade (Gatebe et al., 1996; Gatari et al., 2005; Gatari et al., 2009; Boman, Petersson et al., 2010) and is relatively well known by now, which helps in the interpretation process. To further identify possible long range transport of particles, air mass back trajectories were calculated using the HYSPLIT model (Draxler et al., 2010).

Positive matrix factorization (PMF) was used as a multivariate factor analysis method for identifying the variations in daily contributions of different sources to the particulate composition (Paatero et al., 1994; Paatero, 1997). For the PFM analysis the EPA PMF 3.0 program provided by the U. S. Environmental Protection Agency (Norris et al., 2008) was used. A robust and understandable result of the PMF analysis included five components; mineral dust, biomass
burning, long-range transport of polluted air, traffic and a Cl-rich component. Combining the PFM results with information regarding the weather conditions it is possible to see a clear decrease in the contribution from the mineral dust component during the rainy season in October and November 2008. During the same period the importance of biomass burning as a source of particles increased. Although the traffic in Nairobi is chaotic with very slow traffic flows most of the day and emitting considerable amounts of air pollutants, the biomass influence can clearly be seen during the whole measurement period. From these results it can be concluded that the PMF analysis resolves the identification of particle sources in a good way.

The results of this study proves that the direct and non-destructive analysis of the aerosol loaded filters by EDXRF spectroscopy is an excellent analytical tool for this kind of elemental composition determination.

**Gothenburg, thermal inversion influence**

Part of the large GÖTE-2005 measurement campaign held in Gothenburg, Sweden, was devoted to the study of the elemental content of PM$_{2.5}$ particles. The overall aim of the whole campaign was to study how the urban air quality was affected by thermal inversions during the winter season. Gothenburg’s location in a valley together with the thermal winter inversions gives rise to severe air pollution situations, seriously influencing many of the 500 000 inhabitants of the city. One part of the campaign involving particles was aimed at using EDXRF for elemental determination (Boman, Gatari et al., 2009a). Here PM$_{2.5}$ particles were collected on Teflon filters on a daily basis at an urban background site during February 2005 using the same type of cyclone samplers as described above. The Gothenburg harbor located a few kilometers south west of the centre is the largest port in the Nordic countries. The sea outside Gothenburg is also used for all the shipping traffic to the Baltic Sea and the countries surrounding the Baltic Sea.

The elemental analysis was done with a more powerful version of the same EDXRF spectrometer as described above but with an 80 mm$^2$ Si(Li) detector. Calibration of the spectrometer was done with thin film standard samples from Micromatter (Seattle, WA, USA). Repeated analysis of two aerosol filters having typical sample mass were used to establish that the Coefficient of Variation (CV) was 5% (Molnár, Johannesson et al., 2006). The evaluation of the spectra from the analysis of the samples was performed by the QXAS/AXIL (Bernasconi et al., 2000) software available through the Seibersdorf laboratories of the International Atomic Energy Agency (IAEA).

In the PM$_{2.5}$ samples the concentrations of S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br and Pb were determined. In these samples S, Cl, K, Ca and Fe dominated with average concentrations of 100 ng/m$^3$ or higher. Due to shifting meteorological conditions the concentration variation was large in this study, as was also noted in the Nairobi study. It can also be noted that the average Pb concentration at the site was 6.2 ng/m$^3$, far below the air quality standard (AQS) of 500 ng/m$^3$ indicating that Pb is not a large air quality problem in Gothenburg. The same is true for many European cities, after banning of leaded petrol in the European countries in the eighties.
To determine the possible influence of long range transported pollution episodes the HYSPLTYT model (Draxler and Rolph, 2010) was used to calculate 72 hour back trajectories for the air masses arriving at the measurement site each day of the campaign.

Figure 2. The daily S and Fe concentrations at the background site together with indications of possible source regions. Apart from source areas the inversion period between February 27 and 28 is marked in the figure. Figure from (Boman, Gatari et al., 2009a), by permission of the authors.

Figure 2 illustrates how the combination of elemental concentrations of selected elements and the information of source areas can be used to explain the pollution situation during different days of the measurement campaign. In figure 2 the concentrations of Fe are plotted in black and S in red, with their corresponding Y-axis as a function of date of sample collection. The date in the figure is the date when the 24 hour sampling was started for each sample. By looking at similarities and dissimilarities in the concentrations of Fe and S, together with the outcome of the HYSPLIT back trajectory modeling, different regions can be pointed out as main contributor of these elements during the different days. Very clear air from the Atlantic region as well as substantially more polluted air from Russia and Eastern Europe can be identified in the figure. At the end of the measurement period there was one night with a strong thermal inversion. From the concentrations of Fe and S during this period we can conclude that there are no substantial sources of S in Gothenburg, since the S concentration did not change during the inversion while Fe showed its highest concentration during the inversion. The PM$_{2.5}$ concentration alone did not show the same
variation, and the elemental composition obtained by the EDXRF analysis is needed for source apportionment.

In four campaigns, representing different seasons, PM$_{2.5}$ samples were collected in Skopje, capital city of the Former Yugoslavia Republic (FYR) of Macedonia, between December 2006 and October 2007 (Kovacevik, Wagner et al., 2011). Skopje is located in a valley surrounded by high mountainous areas on the Balkan Peninsula. The location gives rise to repeated periods of stagnant air influencing the air quality in Skopje adversely. Since the winter in Skopje is cold the influence of stagnant air causes severe air quality problems in this season due to emissions from biomass and oil burning for heating. The effect has been seen as an increase in mortality rates in the urban area of Skopje (Kendrovski, 2006). The traffic is another source of pollution, with non-optimally maintained cars and an infrastructure not fully developed for the increased traffic burden. Since Skopje is the largest city in FYR of Macedonia, with 2 million inhabitants, it also houses large industrial areas contributing to the deterioration of the air quality in Skopje.

Sampling was done approximately 2 km from the city centre, 10 meters above street level with a plastic cyclone with the flow rate set to create a particle size cut off of 2.5 micrometers. Polycarbonate membrane filters with a pore size of 0.4 micrometers was used. In this study the filters were exchanged every 12 hours. The concentration of PM$_{2.5}$, the elemental composition and black smoke concentration were used as parameters in an attempt to identify different sources of particles in central Skopje and reveal season variations in the concentrations and composition.

The concentrations of Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb were determined by EDXRF spectroscopy at the University of Copenhagen. In this spectrometer the primary X-ray beam is monochromatised by a Highly Oriented Pyrolitic Graphite (HOPG) crystal. Signals are detected with a Peltier-cooled Si(Li) detector with an active area of 20 mm$^2$. The vacuum used during analysis gives low detection limits for elements all the way down to Si. Pairwise correlations between the elements, BC and PM$_{2.5}$ revealed that some sources, identified by their elemental signatures, had the same correlation throughout the year, while others showed clear seasonal variation. Elements of crustal origin showed good correlations ($R = 0.79$ to 0.97) as did V-Ni ($R = 0.77$) while the correlation between Pb and Zn was lower ($r=0.53$). The correlation between Pb and Zn showed a good correlation during all seasons except during spring, suggesting different sources during the different seasons. Pb and Zn are signs of traffic influence, since Zn can come from both burning of lubrication oil and tire wear and Pb came from the use of leaded petrol, not banned until 2007. Positive Matrix Factorization was used for source apportionment and to quantify the contribution from the different sources. The PMF analysis identified four main sources to the PM$_{2.5}$ particles in Skopje; mineral dust (main observed tracers Si, K, Ca, Ti, Fe, Sr, Rb), combustion (BC, S, K, V, Ni), traffic (Pb, Zn) and a
mixture of sulfate and mineral dust as the fourth component. Wintertime the combustion component is dominating to almost disappear during summer, while mineral dust dominates during summer but is seen all year around. Traffic is also seen all year round with the largest influence in the autumn season. More studies could explain the remaining uncertainties but already now it can be concluded that with the help of the elemental determination using EDXRF the seasonal influence of different sources can be identified.

Stockholm, indoor and outdoor

Since there is another conference presentation focusing solely on the correlation between outdoor sources and indoor elemental concentrations (Godoi et al., 2010), this summary of the penetration factors and seasonal variation of trace elements in PM$_{2.5}$ collected in different environments in Stockholm, Sweden, between December 2003 and July 2004 (Molnar, Bellander et al., 2007) is kept short. In this study indoor and outdoor samples of PM$_{2.5}$ were collected at 40 sampling sites, representing environments where children spend a considerable part of their time, i.e. homes, schools and pre-schools. The aims of the study were to characterize trace element concentrations in the different environments and to compare indoor and outdoor conditions. An additional aim was to search for a correlation between traffic-related trace element concentrations and NO$_2$ concentrations.

Samples were collected on Teflon filters during the winter and spring seasons at each sampling site, using Harvard impactors with a flow rate of 10 L/min. The elemental content of the samples was determined with the laboratory built three axial, secondary target EDXRF spectrometer described above, in the Gothenburg section of the article. Concentrations of S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb were obtained from most of the filters. The concentration of NO$_2$ was measured using passive, diffusive samplers.

Stockholm is considered to be a relatively clean city, which can be seen for example by the fact that only S was above 100 ng/m$^3$ in all the different environments during both seasons. The maximum average Pb concentration in the particles is 100 times lower than the AQS, also indicating a clean environment. Still variations in the Pb concentrations could be observed between the indoor and outdoor environments and depending on season. Pb is an example of a long range transported (LRT) element that together with other LRT elements S, Ni and Br was found to have significantly lower concentrations indoor compared to outdoor. In Table 1 the median infiltration factors for the different environments and seasons are tabulated. From the table it can be concluded that the Swedish homes are relatively well isolated, since the factors are relatively low, especially during the winter season when doors and windows are normally closed. Only during spring and at the pre-schools the concentrations of S and Pb indoors is almost as high as outdoors, probably due to the more open doors as spring arrives.
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**Table 1. Median infiltration factors for S and Pb in the different environments during the winter and spring seasons. Adopted from (Molnar, Bellander et al., 2007).**

In the outdoor samples Cu was found to have a correlation with the NO\textsubscript{2} concentrations. Since Cu is emitted from brake linings it was concluded that a correlation between the elemental tracer Cu and NO\textsubscript{2} from traffic existed, although further studies are needed to verify this conclusion.

**Single particle analysis, source apportionment**

Many different techniques to make elemental analysis of single aerosol particles have been used during the last decades. A summary of the latest advances in the area can be found in the JAAS update articles on XRF (West et al., 2009). We will shortly describe a laboratory technique used by Sun et al (Sun, Liu et al., 2009) where the aim of the study was to do source apportionment, with a potential to be used in other places than in Beijing. In their experiments a polycapillary lens was used to focus the X-ray beam from an ordinary X-ray tube into a microfocused X-ray beam. Using the polycapillary lens a flux density gain of 32600 was obtained. The X-ray source of the spectrometer is a rotating anode generator with an original spot size of 300 x 300 µm which is focused to 33.7 µm. The obtained minimum detection limits in the range of tens of ppm were higher than those obtained by using synchrotron radiation as a source, but were low enough to detect several elements in single aerosol particles.

Samples were collected in Beijing using a cascade impactor with eight stages. In the analysis only the stages with particles between 2 – 4 µm and 0.5 – 1 µm were used. Initially a database of known signatures of single particles obtained by sampling particles from specific sources, for example traffic generated particles, soil and construction dust. To test the suitability to do source apportionment using this single particle analysis technique samples were collected during different days without and with traffic restrictions during the “Good luck Beijing” test before the 2008 Olympic Games in Beijing. During these days only odd or even numbered license plates on the cars were allowed on the streets of Beijing. By comparing the particles identified as emitted by traffic before and during the test, it was shown that the percentage of traffic related particles decreased from more than 30% of the particles to around 20%. It was concluded that this use of a polycapillary lens to gain intensity and focus the beam can be advantageous for single particle analysis, if quantification is not needed.
SUMMARY AND FUTURE PERSPECTIVES

Different setups of the efficient, multi-elemental and sensitive XRF analysis technique have been shown to play an important role in the determination of the elemental composition of minute aerosol particles in urban environments. By combining the elemental information with metrological data, results from complementary analyses and knowledge of possible elemental compositions of particles from different sources it was possible to identify the origin of the elements in different urban environments. The potential of combining the analysis outcome with powerful statistical tools like PMF was demonstrated by the studies summarized here. The elemental determination by XRF and back trajectories proved to be successful combination in the differentiation of contributions to the urban pollution mix from pollutants of local and regional origin in the studies in Gothenburg and in Skopje. This knowledge can be used in other environments influenced by similar weather situations and can thus help decision makers apply appropriate abatements to battle bad urban air quality, a problem facing a large portion of the world’s population and thus of utter importance for a secure and sustainable development of the urban environment.

On a smaller, more local scale the identification of elements in aerosol particles having different infiltration factors, as shown in the indoor and outdoor study in Stockholm, illustrates the problem of applying results to different environments. Finally the Beijing study shows that it is possible to do advanced aerosol studies using laboratory size XRF equipment but the problem lays in both the collection of the aerosol particles and in the large focal point, compared to the particles size.

As outlined in the introduction XRF can be used for a variety of environmental studies, but the examples have been selected with a focus on the urban environment. These selected examples can be used to prove the potential of XRF analysis as a tool in abating a deteriorating urban air quality. This is a problem facing a large portion of the world’s population and thus of utter importance for a secure and sustainable development of the urban environment.

We have described the successful use of EDXRF for elemental determination of aerosol particles. Compared to measurements of gaseous pollutants there is still a lack of easily accessible analysis of single particles with a high time resolution. The concentration of gaseous pollutants can be determined in real time with a few seconds or minutes time resolution. This time resolution is yet to be reached for XRF analysis of particles. Using an aerosol mass spectrometer (Svane et al., 2009) some of the elements in single particles can be determined in fractions of seconds. Although real time EDXRF analysis of single particles are still an issue for the future, an interesting option was identified in a recent paper in Atmospheric Measurement Techniques, Discussion by Yu et al. (Yu et al., 2010). The authors described a fast time-resolved aerosol collector able to collect and identify the location of a collected aerosol particle on the collection substrate with a 4 ms time resolution. Using this collection technique and combining it with EDXRF analysis of the single aerosol particles would make it possible to time stamp the analyzed
particles and thus making a better connection between gaseous and particulate pollution possibly resulting in a better source apportionment and finally increase the possibility to make optimized decisions for a positive development of both our environment and our health.

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