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Abstract. Direct TXRF analysis of nanoparticles deposited on filters was evaluated. Standard filters spiked with known amounts of NP were produced using an atomizer which generates an aerosol from a NP containing-liquid suspension. Polycarbonate filters provided the highest fluorescence signals and black polycarbonate filters containing chromium were further selected, Cr being used as internal standard for elemental quantification of the filter contaminants. Calibration curves were established for various NP (TiO₂, ZnO, CeO₂, Al₂O₃). Good linearity was observed. Low limits of detection were in the tens to the hundreds of ng per filter, the method being less adapted to Al₂O₃ due to the poor TXRF sensitivity for light elements. The analysis of MW-CNTs was attempted by quantification of their metal (Fe) catalyst impurities. Problems like CNT dispersion in liquids, quantification of the deposited quantity and high Fe-background contamination.

1. Introduction

Occupational exposure limits to aerosols do not presently take into account the size of airborne particles [1], although their potential toxicity may well depend on this characteristic, particularly when talking of nanoparticles (NP). Numbers of techniques (Scanning Mobility Particle Sizer (SMPS), Electrical Low Pressure Impactor (ELPI),…) based on dynamic light scattering and/or electric mobility measurements are now commercially available to characterise NP aerosols [2]. Although very useful when the size distribution of the NP population is to be instantaneously estimated, they are not suited for continuous follow-up of the exposure of workers handling specific engineered NPs; information on the chemical composition of the particles is required to discriminate them from the ambient background.

For such purpose, a two-step method can be proposed, which consists in first collecting the particles on filters, and then analysing the deposited particles by an elemental analytical technique. Several kinds of sampler devices are commercially available and have been tested for their efficiency [3]. They all showed satisfactory performances, although some loss of particles could be observed on the inner wall of non-treated polystyrene cassettes.
Various techniques can be proposed to achieve the second step-analytical challenge, among which Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These elemental techniques need time-consuming sample digestion steps prior to analysis that may contaminate the sample, particularly with omnipresent elements like aluminium and zinc [4]. Furthermore NP containing elements like refractory metals and metalloids may not be fully dissolved leading to poor recoveries.

More recently, Total reflection X-Ray Fluorescence (TXRF) has been applied to environmental analyses [5-13]. TXRF is a surface and near-surface multi-elemental spectro-chemical analytical technique [14] which makes it an interesting alternative particularly well-suited here, provided that the NPs deposited on the filters can be analysed without any extra sample-handling. However, most applications include pre-treatment of the filter, whether by a separate acid digestion [5,6,8,11] or by cold plasma ashing directly on the sample carrier [7,10]; as with other techniques that require sample preparation, contamination problems were reported [11] as well as loss of material [12]. An interesting alternative was proposed by some authors [9,13]: it consists in collecting the aerosol particles by impact on a polished Si or quartz carrier that could subsequently be analysed by TXRF with no further treatment. However, impaction methods require that the carrier be coated with grease to avoid bounce-off effects and use of Si-based carriers may be too expensive for a wide use of this technique.

Recently, Bontempi et al. [12] have investigated the possibility of analysing the chemical composition of atmospheric aerosol particles by TXRF directly on the collection filter. This is an interesting alternative of characterization since it is not destructive and allows subsequent analysis of the filter by other techniques, typically scanning electron microscopy (SEM). They have proven the effectiveness of such simplified procedure that gives higher signal intensities compared with the usual procedure (liquid deposition of a few µl of the digested filter on a quartz glass sample carrier). Recommendations concerning the positioning of the filter in the TXRF chamber must be followed (it must be inserted in a very flat manner) and limitations concerning quantification were set due to the lack of internal standard.

In the present study, we propose a method of characterization and quantification of the chemical composition of particles sampled on a filter by direct TXRF measurement.

2. Experimental

The filters on which NP were deposited were from Millipore or Whatman. All metal oxide NPs were from commercial aqueous suspensions: TiO$_2$ (Mixture of rutile and anatase) was purchased from Aldrich; ZnO was from Evonik, Al$_2$O$_3$ (BA15, α-form) was from Baikowski and CeO$_2$ was from Rhodia. MW-CNT (Graphistrength C100 from Arkema) were crushed by the supplier and used as received. Their average diameter was 10-15 nm; the length was less than 10 µm. They contain impurities from catalyst residues: 2.3 % Al and 1.9 % Fe on a weight basis. Ultrapure (UP) water was used throughout of the study; it was obtained from a MilliQ system (Millipore).

The NP suspensions were prepared by weighing a known amount of commercial NP powder or concentrated suspension in a known volume of UP water. Dispersion was assured by ultrasound treatment (2 – 5 min) prior to each atomisation procedure. Concentrations of 1 mg/l or 10mg/l of metals were used for metal oxide NPs. Because of the low metal content of MW-CNT, suspensions with higher concentrations were prepared with these NPs (280 mg/l MW-CNT).

The system set up to produce standard filters containing known amounts of NP is given in figure 1. A constant output atomizer (TSI, model 3076) equipped with a diffusion dryer (TSI, model 3062) was used to produce aerosols from NP dispersed suspensions. The nano-aerosol was generated in a flow stream of purified air and then passed through a filter membrane embedded in a cassette sampler (25 mm polypropylene conductive black from SKC Omega, including a support pad). The air flow rate was measured by a thermal mass flowmeter (TSI, model 4000).

The generated aerosol was characterized with the help of a Scanning Mobility Particle Sizer (SMPS Grimm, series 5400): their particle size distribution was measured, based on electrical-mobility particle size classification. The total mass deposited on the filter was calculated as the mass-based size
distribution given by the SMPS (knowing the density of the tested particles) times the flow rate times the duration of exposure.

![Diagram of experimental setup](https://via.placeholder.com/150)

**Figure 1.** Experimental set-up for the preparation of standard filters.

The spiked filters were then withdrawn from their cassettes and analysed with a benchtop Total reflection X-Ray Fluorescence spectrometer (TXRF NanoHunter from Rigaku) featuring two different X-ray tubes (Cu and Mo). The sample spectra were collected for 200 s with an angle of the incident beam set at 0.75 °. A special carrier was designed in order to set the filter in a flat position beneath the detector so that no hindrance occurs and its surface be hit by the low glancing angle incident X-rays. No other specific handling was needed.

For the in-situ sampling procedure in an alumina manufactory, a portable sampling device was used to collect the ambient airborne particles generated during grinding and sieving operations. The air flow rate was 0.9 l/min.

### 3. Results and discussion

3.1. Homogeneity of the deposition

Personal devices used for exposure monitoring are traditionally based on a portable vacuum pump that draws air up through a filter embedded inside a special leak-free holder. Such design ensures that collection of the particles be homogeneous throughout the surface of the filter. Consequently, depositions made on purpose for our application should be as homogeneous as possible to mimic the usual procedure.

Two ways have been investigated. First, a liquid deposition of an aqueous NP suspension of known concentration was carried out on the filter. After drying, clogging of the particles would always occur, as illustrated for CNTs in figure 2.a. Second, an aerosol was generated from an aqueous NP suspension (with the help of a constant output atomizer) and sprayed through the filter.

![Image a) and b)](https://via.placeholder.com/150)

**Figure 2.** Two MW-CNT deposition processes on filters. a: liquid deposition. b: aerosol deposition
With this configuration, homogeneous deposition was observed (figure 2.b), confirming that only the atomization process would be useful when dealing with direct measurement of the filter surface by TXRF.

3.2. Choice of the filter
The first condition the filter should meet is efficiency. Indeed, nearly all fibrous and sponge-like structure filters would meet this requirement as Brownian motion favours interception and diffusive deposition of the particles on the fibers. Polycarbonate (PC) membranes do not show the same structure (they are made of plain material with calibrated poreholes) and their efficiency was to be confirmed.

Penetration tests were conducted on various filters with different pore sizes. Figure 3 shows that, for all kinds of filters that were tested, the efficiency is higher than 99.5 %, whatever the size of the particles, limited to 300 nm in diameter.

Figure 3. Efficiency of various filters towards NP retention. Porosity is indicated in the legend.

The second condition the filter should meet is reflectivity. Indeed, the smoother the surface of the substrate, the higher the sensitivity of the fluorescence signal. Various filters have been tested to check this property. Each of them was spiked with TiO$_2$ NP (14 µg/cm$^2$ of Ti) generated by the aerosol technique. The TXRF signal for Ti is reported in figure 4.

Figure 4. Ability of the filter material to be a sensitive TXRF substrate
The best sensitivity was obtained with polycarbonate filters (by at least one order of magnitude compared with the second best candidate). Fibrous or sponge-like materials like mixed cellulose ester, PVDF, PTFE or Nylon show a rough surface structure that allows the NP penetration deep into the filter thickness. On the contrary, polycarbonate filters show a smooth and flat surface with calibrated porholes. Nanoparticles are deposited mainly on the reflective surface; they are hardly incorporated within the filter material, except for those that pass through the pore holes and are deposited on the pore surface. Both aspects (smooth surface and limited incorporation inside of the substrate) account for the high level of signal obtained with polycarbonate.

3.3. Calibration
Quantification of the deposition was first attempted with white PC filters, by plotting the TXRF signal of the element of interest (deposited as NPs) as a function of the quantity deposited on the filter. The signal was dependent on the deposited quantity of NP but the data were somewhat scattered. Black polycarbonate filters were also tested. Because of the occurrence of chromium in their PC matrix (figure 5), an attempt to use this constitutive element as internal standard was proposed.

![TXRF spectrum of a black PC filter spiked with ZnO NP (0.3 µg/cm² Zn). Filter: black PC; porosity: 0.4 µm; diameter 25 mm.](image)

Figure 5. TXRF spectrum of a black PC filter spiked with ZnO NP (0.3 µg/cm² Zn).

Filter: black PC; porosity: 0.4 µm; diameter 25 mm.

Figure 6 gives an example of the calibration curves that were obtained either considering the gross signal for Zn (Figure 6.a) or including the Cr correction and plotting the signal ratio Zn/Cr (figure 6.b). Linearity is better in the second case, showing that Cr contained inside of the filter matrix can account for the differences in the positioning of the filter surface under the detector.

![Calibration curves for Zn by direct TXRF measurements on PC filters spiked with ZnO NP.](image)

Figure 6. Calibration curves for Zn by direct TXRF measurements on PC filters spiked with ZnO NP.
a: without correction for Cr. b: with correction for Cr.
Filter: black PC; porosity: 0.4 µm; diameter 25 mm.
3.4. Quantification of NP / limit of detection

Standard filters were prepared by aerosol deposition of increasing amounts of various NPs. ZnO, TiO$_2$, CeO$_2$, Al$_2$O$_3$ and MW-CNT were tested.

Figure 7 gives the calibration curves for the metal oxide NPs. Ti, Ce, Si and Al were analysed with the Cu-X-ray tube while Zn was analysed with the Mo-X-Ray tube. In all cases, Cr was analysed with the same X-ray tube as that used for the element of interest.

![Graphs showing calibration curves for different metal oxides](image)

**Figure 7.** Calibration curves for a: TiO$_2$, b: ZnO, c: CeO$_2$ and d: Al$_2$O$_3$.

Filter: black PC; porosity: 0.4 µm; diameter 25 mm.

Good sensitivity was obtained for Ti, Zn, and Ce. Low limits of detection (LLD) for these elements were calculated as three times the standard deviation of the background signal of 6 different bare filters from the same batch. They are gathered in table 1.

| Particle | ng of element / cm$^2$ | ng of particles / filter |
|----------|------------------------|--------------------------|
| TiO$_2$  | 5                      | 38                       |
| ZnO      | 10                     | 58                       |
| CeO$_2$  | 26                     | 159                      |
| Al$_2$O$_3$ | 80                  | 737                      |

TXRF is not a sensitive technique for light elements; it is therefore not appropriate for trace analyses of Al, as revealed by the calibration curve in figure 7d. The LLD for this element is significantly higher than for the other metal oxides.
Atomisation of a CNT suspension was undertaken using the same procedure as that used with metal oxide NPs. The visual aspect of the suspension included agglomerates; the suspension was not steady and clogging of the atomizer head would occur after a few hours of continuous aerosol generation. Such instability has already been observed for CNTs [15] with this type of aerosol generation [16] and is essentially due to the high hydrophobic properties of these particles that favours their clustering.

A first series of CNT-spiked PC filters was analysed by TXRF. Carbon is too light to be analysed by TXRF. Hence, CNTs are spotted looking at Fe, the metallic catalyst. CNT concentration-dependent Fe signal was obtained (figure 8). However, due to the omnipresence of this element in the environment, the data are very scattered and the background level is high.

![Figure 8. Calibration curve for Fe-containing CNTs](image)

Furthermore, a second series was prepared and did not show concentration dependence calibration curve. It was suspected that segregation might occur by preferential sedimentation of the Fe-containing CNTs (of higher density) over those without catalyst. Further investigations need to be undertaken in order to assess the relevance of this elemental analytical method applied to such

4. Limitations
One of the trickiest points here is the preparation of standard filters. Particularly, evaluation of the deposited quantity is not obvious. At present, it is ensured by SMPS measurements. This technique is based on electrical mobility properties of the particles and gives access only to their equivalent diameter, considering that particles be spherical. However, for a number of NPs, this equivalent diameter is not representative of their real size. This is particularly true for specific morphologies like needles or tubes and models have been proposed to try to convert the electrical mobility size given by SMPS measurements to that of cylindrical particles [17]. It was found that the cylindrical particles have a significantly smaller volume than the spherical particles with similar mobility. Further investigations must thus be undertaken to evaluate the concentration of particles deposited on standard filters more precisely.

5. Conclusions
The method proposed here is an interesting alternative to conventional analytical procedures that require time-consuming and potentially contaminating sample treatments. The feasibility of the chemical detection of metallic particles directly on filters was demonstrated using TXRF and PC filters for good reflectivity. Semi-quantification was established for a number of nanoparticles (TiO₂,
ZnO, CeO$_2$) with low limits of detections in the tens to hundreds of particle ngs per filter, except for light elements like Al that shows poor sensitivity inherent to the method. Evaluation of the deposited quantity, as measured by SMPS, still needs to be clarified, and particularly size response of such aerosol characterisation device need to be checked, with ICP-MS controls, for instance.

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