

A comparison between PIXE and ICP-AES measurements of metals in aerosol particulate collected in urban and marine sites in Italy



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ABSTRACT

PIXE and ICP-AES techniques are largely used in atmospheric aerosol studies. Since PIXE is able to provide the total elemental concentrations, while ICP-AES results depend on the extraction conditions, parallel PIXE and ICP-AES measurements of Fe, Al, Cu, Pb, Mn, Cr, Ni, V, As on PM10 and PM2.5 samples were compared. Two extraction procedures were applied to samples from 5 sites at different anthropization level in Italy: a “weak” extraction (HNO₃ at pH = 1.5) and a “strong” extraction (micro-wave oven in HNO₃ and H₂O₂ – following EU rules).

The amount of the metal extracted in the different conditions resulted to be strongly dependent on the sampling site, on the main sources of the particle (crustal or anthropic) containing the metal and on the sampled size class.

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1. Introduction

Particle Induced X-ray Emission (PIXE) is a suitable technique for analyzing aerosol samples [1–3] due to its ability to carry out a multi-elemental analysis of the particulate deposited on the filter surface without any solubilization procedure, therefore shortening the analysis time and reducing the sample contamination risk. Unlike PIXE, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) results depend on the extraction conditions (extracting solution composition, pH, temperature, pressure, contact time). The metal fraction extracted in weaker conditions is more “available” for the natural systems; in this way, it is possible to better evaluate the impact of heavy metals on the environment and the human health.

Here, we present some results obtained by comparing PIXE and ICP-AES measurements carried out on PM10 and PM2.5 aerosol samples, collected in five sites in Italy characterized by different sources and anthropic impact. The metal fractions solubilized in different extraction conditions were calculated taking the PIXE values as 100% of the metal. Two extraction methods were used: (1) sonication in HNO₃ at pH = 1.5 at room temperature; (2) micro-wave oven extraction in conc. HNO₃+H₂O₂ mixture. The goal was

to quantify the dissolved fraction of each metal as a function of the aerosol sources and size classes.

2. Sampling and analysis

2.1. Sampling sites

PM10 and PM2.5 24-h samples were collected by low-volume (2.3 m³/h, EU rule EN 12341) samplers on Teflon filters (Pall Teflo R2PJ047) in 5 sites (in brackets, the main local aerosol sources are listed):

VSL (Villa San Lorenzo) – Suburban site (traffic, regional airport, domestic heating, shopping malls, light industrial activities), 10 km N–W of Florence (Italy). From Sept. 2005 to Dec. 2006, 263 PM10 and 263 PM2.5 samples were collected.

FIB (Firenze Bassi) – Suburban site (traffic, domestic heating), 5 km N–E of Florence. From Mar. 2009 to Mar. 2010, 60 PM2.5 samples were collected.

FIG (Firenze Gramsci) – Heavy-traffic site (traffic, domestic heating), located in the centre of Florence (Italy). From Mar. 2009 to Mar. 2010, 60 PM2.5 samples were collected.

LMG (Livorno MauroGordato) – Marine coastal – urban background site (primary and secondary marine aerosol, harbour emissions, heavy petrochemical industry), located 5 km from the coast line (Tyrrhenian Sea) in a park near Livorno (Tuscany, Italy). From Mar. 2009 to Mar. 2010, 60 PM2.5 samples were collected.

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LPD (LamPeDusa Island) – Marine site in the Southern Mediterranean Sea, Sicily Channel (primary and secondary marine aerosol). From Dec. 2004 to Dec. 2008, 670 PM10 samples were collected.

2.2. PIXE analysis

PIXE analyses were performed at the 3 MV Tandetron accelerator of the INFN-LABEC laboratory, with an external beam set-up [4]. Each sample was irradiated for ~5 min with a 3.2 MeV proton beam (~2 mm² spot, 5–50 nA intensity). A filter scanning was carried out to analyze most of the deposit area.

PIXE spectra were fitted using the GUPIX code [5] and elemental concentrations were obtained by a calibration curve from a set of thin standards of known areal density (Micromat Inc.).

2.3. ICP-AES measurements

Measurements were carried out by a Varian 720 ES simultaneous ICP-AES equipped with a CETAC U5000 AT+ ultrasonic nebulizer. Two extraction methods were used:

- 0.1% sub-boiled distilled (s-b d.) HNO₃ (pH = 1.5) in an ultrasonic bath for 15 min at room temperature. This fraction represents the most “available” metal fraction (including free metal, labile complexes, carbonate and bicarbonate salts), considering the pH = 1.5 as the lowest limit for “natural” pH values [6].
- Conc. s-b d. HNO₃ and 30% ultrapure H₂O₂ in a microwave oven, at 220 °C for 25 min (*P* = 55 bar), according with the EU rule EN 14902 (2005) for As, Cd, Ni and Pb determination.

Daily calibration standards (internal standard: 1 ppm Ge) were used for quantification.

3. Data discussion

The comparison between PIXE and ICP measurements enlightens the capability of a metal to be mobilized in natural matrices, therefore evaluating its impact on the environment.

3.1. Comparison with PIXE – extraction with HNO₃ at pH 1.5

3.1.1. LPD site

The PIXE and ICP (HNO₃ at pH 1.5) measurements of selected metals (Fe, Al, Cu, Pb, Mn, Cr, Ni, V and As) were compared in

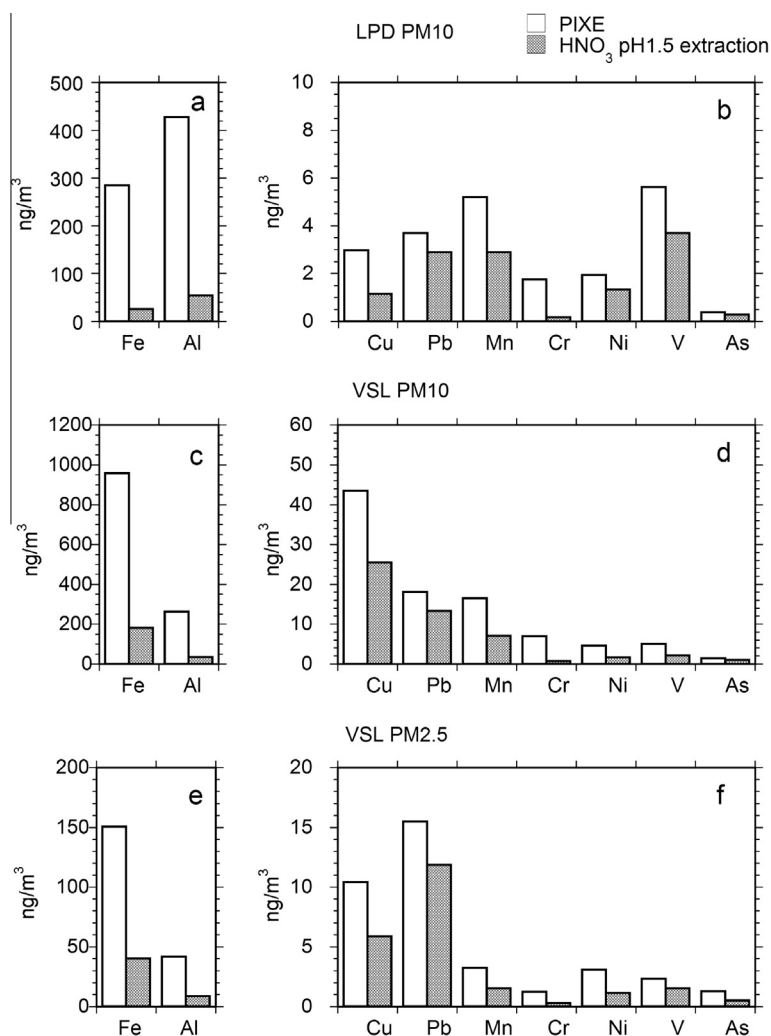


Fig. 1. Mean concentrations of selected metals determined by PIXE (white columns) and ICP-AES following the extraction procedure with HNO₃ pH1.5 in ultrasonic bath (grey columns) for three different samples: LPD PM10 (panels a and b), VSL PM10 (panels c and d) and VSL PM2.5 (panels e and f).

aerosol samples collected at the LPD (PM10) and VSL (PM10 and PM2.5) sites.

Fig. 1a and b shows the LPD PM10 metals mean concentrations. Beside marine emissions, continental dust is a significant source for the LPD aerosol; indeed, crustal oxides mean annual contribution is about 17% (w/w). The background contribution of local dust sources is highly enhanced by frequent and large Saharan dust depositions. Due to the dominant contribution of the dust source, the anthropic emissions have a negligible impact on the main metals (especially Al, Fe and Mn), as shown by their very low enrichment factors (E.F.). In particular, the mean Fe/Al ratio (0.68 w/w) settles exactly on the value of the Earth's crust ratio (0.68 w/w [7]). On the contrary, the quite high mean concentrations of V (5.8 ng/m³) and Pb (3.7 ng/m³) can be attributed to anthropic emissions (see below).

Since Fe and Al are mainly contained in crustal matrices, their extractable fraction at pH = 1.5 is low (9.1% and 13%, respectively, values roughly representing the carbonate contributions). The Fe concentrations measured at pH 1.5 deserve a particular attention in order to evaluate the metal fraction available for marine organisms in a short time after the deposition of massive Saharan dust on the sea surface. Indeed, the possible role of Fe in the fertilization of high-nutrient, low-chlorophyll (HNLC) areas largely depends on the concentration of dissolved Fe and not on its total quantity. The role of Fe as a fertilizing agent in the Mediterranean Sea is still under debate; indeed, the frequent Saharan dust deposition events could deliver to the sea surface an amount of Fe, as well as other nutrients (Al, Mn, Zn and Pb), large enough to assume that Fe is not a limiting factor [8]. Nevertheless, Bonnet and Guieu [9] reported that Fe concentration in superficial layers showed a depletion after spring blooms in the Western Mediterranean Sea. A reliable evaluation of the Fe available fraction in the LPD area could give further insights to this discussion.

Unlike Al and Fe, high extraction efficiencies at pH 1.5 were observed for heavy metals with a relevant anthropic contribution: Pb (79%), Ni (69%), V (67%) and Cu (38%). Large Pb soluble fraction can be explained by the combustion of fuels containing Pb in weak complexes, such as soluble organometallic compounds [10]. V and Ni, markers of specific anthropic emissions (combustion of heavy fuel oils – HFO – occurring in oil refineries, thermo electrical plants and large ship engines), deserve a particular attention, because ship emissions represent a significant contribution to the LPD PM10 [11]. Indeed, V and Ni show a different behavior in the LPD aerosol as a function of their sources. Several soluble compounds, such as sodium vanadates and nickel hydroxides, are formed during HFO combustion [12]. In the HFO-combustion enriched samples, the V and Ni soluble fractions are 80% and 77%, respectively [11]. On the contrary, V and Ni present as oxides or contained in the silica matrix show a lower solubility (36% and

45%, respectively [11]). As a consequence, the anthropic emissions of V and Ni have a larger impact on the marine biological cycles.

3.1.2. VSL site

At this more anthropized site, the metal absolute and relative concentrations show a very different pattern (Fig. 1c and d). Total Fe concentrations are definitely higher than Al ones (960 and 260 ng/m³, respectively), resulting in an E.F. of about 5.4, with respect to the Earth's crust mean composition. Even trace metals show higher mean concentrations in the VSL aerosol (Fig. 1d), with respect to LPD (Fig. 1b), especially Cu (VSL/LPD = 14) and Pb (VSL/LPD = 5).

As far as the soluble fraction is concerned, Al, Fe and Mn show low percentages (13%, 19% and 43%, respectively), despite the large anthropic contribution at least for Fe. Anyway, combustion processes emit Fe mainly as oxide species, not soluble in HNO₃ at pH = 1.5 and room temperature. In spite of the low percentage of the Fe soluble fraction, this value is about 2 times higher than that measured at LPD (9%), pointing out a larger contribution of labile Fe species or free metal from anthropic sources.

High percentages of the soluble fraction were measured for Pb (74%), As (66%) and Cu (59%). These values are similar (Pb and As) or even higher (Cu) than the ones measured at LPD. On the contrary, V and Ni show percentages (41% and 36%, respectively) markedly lower than the LPD values, because the HFO combustions are not relevant at VSL.

At VSL, PM2.5 was also sampled. The PM2.5 metal fractions solubilized at pH 1.5 are similar or higher than those measured in the PM10 (Table 1). In particular, the percentages rise to 77% for Pb and 65% for V. An apparent anomalous value is shown by As: 39% in PM2.5, instead of 66% in PM10. However, it has to be noted that the As detection limit for PIXE is high (around 0.3 ng/m³) and many samples show As concentration lower than this value (annual mean around 1.0 ng/m³). Therefore, the ICP/PIXE ratios were calculated on a small data set and could be affected by larger uncertainties, thus preventing a reliable evaluation of the As soluble fraction. A similar high data dispersion was also observed for the As soluble fraction calculated by the ICP (HNO₃ and H₂O₂)/PIXE ratio (see later).

It is interesting to note that also the soluble fraction of Fe and Al significantly increases passing from PM10 (19% and 13%, respectively) to PM2.5 (27% and 20%, respectively). This clearly shows that smaller particles contain species more efficiently mobilized in the environment.

3.2. Comparison with PIXE – extraction with HNO₃ + H₂O₂

As concerns such comparison, only a few data are available in literature. Menzel et al. [12] compared the determination of metals

Table 1
Percentage of mean solubility in HNO₃ pH1.5 and HNO₃–H₂O₂ in PM10 and PM2.5 samples collected in the different sites. Mean solubility is calculated from the ratio of mean values.

	LPD PM10	VSL PM10	VSL PM2.5	LMG PM2.5	FIB PM2.5	FIG PM2.5
	Mean HNO ₃ pH1.5 solubility %	Mean HNO ₃ pH1.5 solubility %	Mean HNO ₃ pH1.5 solubility %	Mean HNO ₃ –H ₂ O ₂ solubility %	Mean HNO ₃ –H ₂ O ₂ solubility %	Mean HNO ₃ –H ₂ O ₂ solubility %
Fe	9	19	27	99	98	92
Al	13	13	20	67	76	81
Cu	38	59	56	102	94	107
Pb	79	74	77	84	90	91
Mn	56	43	47	83	85	90
Cr	10	10	24	33	76	82
Ni	69	36	36	106	117	138
V	67	41	65	74	66	65
As	70	66	39	77	130	75

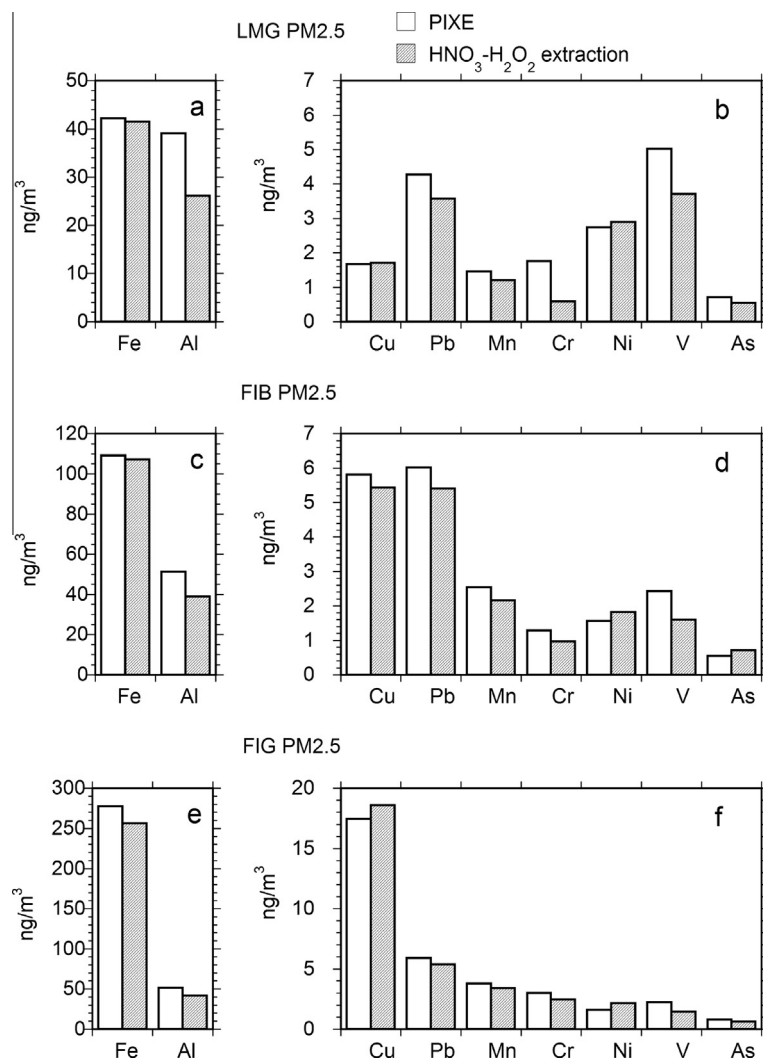


Fig. 2. Mean concentrations of selected metals determined by PIXE (white columns) and ICP-AES following the extraction procedure with HNO₃-H₂O₂ in microwave oven (grey columns) for PM_{2.5} samples collected in three different sites: LMG (panels a and b), FIB (panels c and d) and FIG (panels e and f). The anthropic contribution affecting the sites increases from top to bottom of the figure.

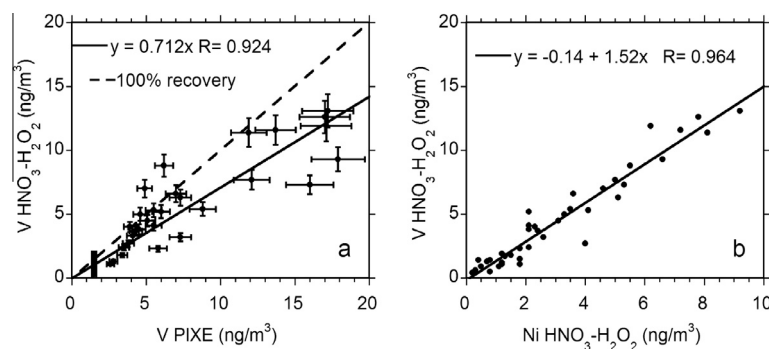


Fig. 3. Correlation between V concentrations in PM_{2.5} fraction sampled at LMG as determined by ICP-AES with HNO₃-H₂O₂ extraction and by PIXE (panel a). Correlation between V and Ni concentrations in the PM_{2.5} at LMG, both determined by ICP-AES with HNO₃-H₂O₂ extraction (panel b).

(Ca, Mg, Fe, Al, Ni, Cu, Ti, Pb, K, Zn, Mn, Cr, Co) and non-metals (Si, P, S, Cl, Br) on TSP (total suspended particulate) samples. The extraction for ICP-AES was performed by a quartz ashing digestion in HNO₃. PIXE and ICP-AES data revealed a good agreement (10–15%) for all the elements, due to the strong solubilization conditions. Saitoh et al. [13] analyzed an urban particulate reference

matter (NIST SRM 1648) by PIXE, ICP-MS and ICP-AES, with a HNO₃ digestion in microwave oven. They found a full recovery for anthropic metals, like Pb, As, Ni and Cu (107%, 120%, 96% and 93%, respectively), and good recoveries for metals with a mixed anthropic-crustal origin, such as Al (83%), Fe (86%) and Mn (86%). A similar percentage (85%) was also found for V.

A recent European regulation (EN 14902, 2005) recommends a specific protocol for the extraction of As, Cd, Ni and V in PM10 samples. We applied the same protocol also to the PM2.5 samples, because this size class is earning a rising interest as a reference parameter for the air quality in urban sites. Indeed, PM2.5 is more affected by anthropic aerosol, especially emitted from productive activities, vehicular traffic, domestic heating and power generation plants. Since in urban areas the crustal input (especially in silicic matrices) is far less abundant in PM2.5 fraction, a higher recovery by ICP-AES is expected, even taking into account the higher strength of the $\text{HNO}_3\text{--H}_2\text{O}_2$ extraction.

The PM2.5 soluble fractions in the three sites were interpreted as a function of the different (qualitatively and quantitatively) contributions of the anthropic sources.

The different anthropic impact is clearly shown by the progressive increase of the total concentration of almost all the elements, with the exception of Al and V (see later), passing from LMG to FIB and to FIG site (Fig. 2). In particular, the Fe/Al ratio (annual mean) is 1.1 at LMG (E.F. = 1.6), whereas Fe becomes the dominant metal in the FIG PM10 (E.F. = 6.5). V and Ni shows an opposite behavior, with concentrations 2 times higher at LMG, with respect to FIB and FIG. The high V and Ni values at LMG are explained by the proximity (about 6 km) to an oil refinery plant and a commercial and touristic harbor.

In all the three sites, the metal fractions extracted by the $\text{HNO}_3\text{--H}_2\text{O}_2$ method are very high, close to $100 \pm 20\%$ (considering the cumulative uncertainties in PIXE and ICP measurements), for almost all the measured elements. Differences among the sites are observed for Al, As, Cr and V.

As expected, an incomplete extraction was observed for Al, because it is present in crustal dust as insoluble silicates and inert oxides. In fact, the LMG background site shows lower recovery (67%) than the urban sites (FIB = 76%; FIG = 81%), where anthropic sources enrich the PM2.5 with more soluble Al species.

Arsenic recovery shows a large variability (FIG: 75%, FIB: 130%, LMG: 77%). Such a variability, as previously noted, could be due to the large cumulative uncertainties of the analytical methods; indeed many samples showed As concentrations below the PIXE detection limit.

Cr shows soluble fractions around 80% in the Florence sites and a far lower value at LMG (33%). Such a pattern could indicate that Cr is present in different chemical species in the Florence and Livorno sites, but further work (especially single-particle geochemical analysis) is necessary to confirm this interpretation. A low Cr soluble fraction (about 25%) was also found in the fly ashes from a biomass gasifier [14]. Anyway, it has to be noted that a large number of LMG samples have Cr concentration below or around the PIXE detection limit; therefore, the evaluation of Cr soluble fraction could be affected by a cumulative uncertainty similar to that observed for As.

Vanadium shows extraction percentages lower than 80% in all the three sites (FIG: 65%, FIB: 66%; LMG: 74%). The larger solubility at the LMG site is justified by the emission from HFO combustions (ship engines) and from an oil refinery plant, where V is present as soluble porphyrin complexes [10]. Indeed, in this site, we measured a very good correlation between soluble V and total V with

a relevant number of samples showing extraction percentages close to 100% (Fig. 3a, dashed line). The very good correlation between V and Ni (Fig. 3b), the latter being another marker of heavy oil refining and HFO combustion, supports the relevance of these sources at LMG.

4. Conclusions

The comparison between PIXE and ICP-AES measurements showed some relevant insights on the different metal availability in different extraction conditions.

In weak extraction conditions (with HNO_3 at pH 1.5), metals mainly arising from anthropic sources show higher solubility than the crustal ones. When PM10 and PM2.5 were sampled in the same site, metals in PM2.5 show a higher soluble fraction, since anthropic sources are dominant.

The stronger extraction procedure with HNO_3 and H_2O_2 (EN 14902 rule) allows the extraction of almost all the metals in the PM2.5 in sites with different contribution of anthropic and natural sources.

As a conclusion, this work shows that ICP-AES and PIXE are complementary techniques and their combined use is able to give powerful information on chemical speciation of metals in the PM.

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