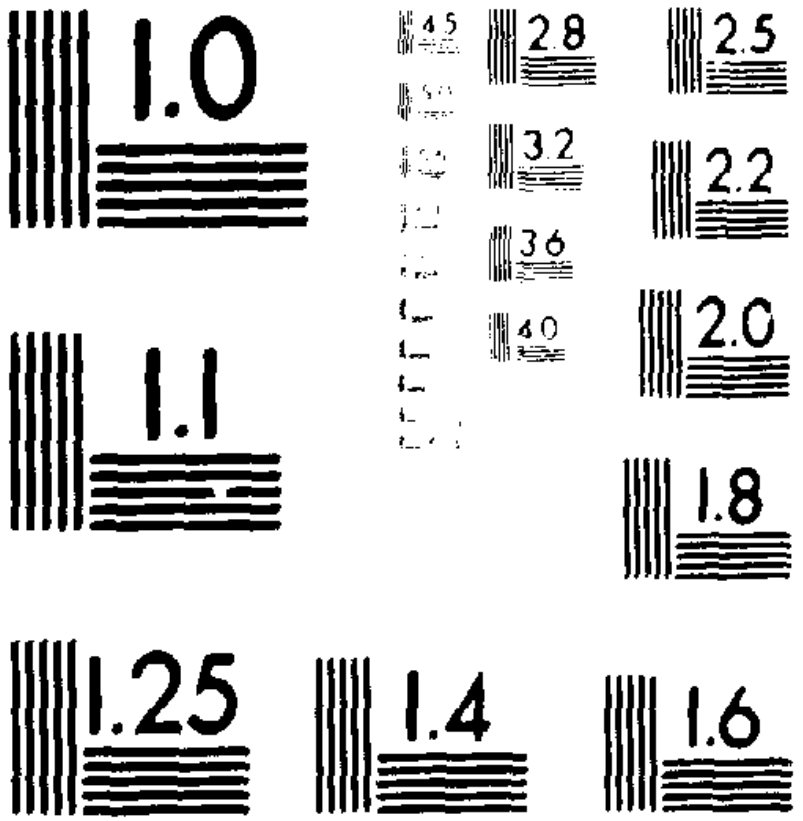

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PIXE ANALYSIS OF TREE LEAVES AS A POSSIBLE COMPARATIVE INTEGRAL MONITOR OF PARTICULATES IN URBAN AREAS

A.Zucchiatti [1], H.J.Annegarn [2] and R.Chisci [3]

(1) Istituto Nazionale Di Fisica Nucleare - Sezione di Genova
(2) Wits-CSIR Schonland Research Centre for Nuclear Sciences
University of the Witwatersrand - Johannesburg
(3) E.O. Ospedali Galliera Genova

ABSTRACT The possibility of obtaining integral comparative data for particulate distributions in urban areas from PIXE analysis of tree leaves is discussed in relation to the leaf gross anatomy, to the diffusion of selected tree species in such areas and to the implementation of experimental techniques necessary to make PIXE analysis effective. Multielemental scans were performed on a small set of samples; results are compared to PIXE analyses of typical urban aerosols. The validity of the method and the criteria for yearly relative comparisons of different areas are discussed.

INTRODUCTION

Multielemental analysis by particle induced X-ray emission (PIXE) is a well established and largely adopted technique. While its most developped application is to the detection of sub-nanogramme quantities of particulates uniformely deposited on inhert substrates by filtration or impaction of particles in aerosols, many are the applications of PIXE to the analysis of non specific samples. PIXE analyses have been carried-on for example on fossilized bone fragments[1], rock specimens[2] and organic tissues (like lung sections, tooth enamel, cardiac tissue) giving at least qualitative information on the trace composition of such materials and in most cases also rather reliable quantitative results, made possible by sofisticated deconvolution codes[3] that are capable of considering even the large self absorption effects in massive samples. We have envisaged the possibility of using the particulate deposition over the surface of leaves to identify the elemental composition of aerosols, by means of an experimental approach that requires to operate the PIXE chamber under a helium atmosphere to avoid the dramatic problem of sample overheating, to retain the volatile parts of the sample, while having little effect on the proton beam itself and on the absorption of X-rays in the chamber. The scope of this report is to discuss characteristics of tree leaves suitable for PIXE analysis, to demonstrate them in the qualitative interpretation of results on a small exploratory set of samples and to discuss the possibility of a quantitative interpretation of the data.

THE LEAF AS A PARTICULATE SUBSTRATE

We shell first review some of the peculiarities of the holm oak (*Quercus Ilex*) tree that make it, in our opinion, a suitable tree species for an exploratory investigation of our proposed method. Some of its peculiarities were considered in relation to the fact that our tests were conducted in the town of Genova, some other were related to the gross anatomy of its leaves. This tree is quite robust, requires little maintenance, is therefore common in municipal gardens and widespread in any part of town. It is classified as an evergreen tree since the leaves have a lifetime of two-three years. It looks therefore possible to perform yearly averages of the deposition of particulates over the surface of leaves, to include in the analysis all microclimate conditions and the very important seasonal variation of wind that in the Genova coastal region blows preferentially from NNE NE in winter months and from S SSW in summer months. Almost one third of the foliage is replaced regularly every year. New leaves appear in spring around march-april to assume adult aspect by may-june while old leaves fall from around mid june to mid september (earlier or later

according to whether the summer climate is dry or wet). This means that collecting leaves in march-april, as we did, allows to choose between one year old leaves and two to three years old ones. The age is easily determined by even a superficial analysis. Young leaves are in fact soft, light green and the margins are entire. One year leaves are coriaceous, green with sinuate margins and display no sign of decay over the surface. Two or three years old leaves tend to be dark green or brown, have usually broken margins and show patches of fisiological decay over the surface. It is possible to collect them, as we did, at an height of about two meters at the bottom of the tree where they should have been rather protected from heavy rains and where particles in the coarse and fine stage should be equally present.

Few anatomic characters make, in our opinion, these leaves quite suitable for particulates collection. The upper surface of the leaf is relatively smooth and coated with some lubricating substances secerned by the leaf epidermis. These lubricants can well exert the same trapping action that paraffin or vaseline exert on standard PIXE impactors to prevent particle bounce-off. The lower part of the leaf is characterized by a dense down that, at a microscopice view, appears quite efficient in trapping particles. Figures 1 and 2 show respectively the upper (sample 8) and lower (sample 9) surface of a leaf collected in an industrial and highly inhabited suburb, as they are seen enlarged 32 times. The large presence of coarse particles reveals the relevance of pollution in that area. A classification of particles according to their diameter has been done and is reported in figure 3 for samples 8, 9, 18 and 19 collected in two spots, one in an industrial area and one in a central area. Although the resolution of our instrument does not allow to resolve particle diameters below 2 μm, it seems however that the range of particle sizes for which the leaf is an efficient substrate can be quite large. In addition one has to consider that accumulation of pollutants by the leaf takes place also through the respiratory process. This is accomplished by apertures (stomata) of $8 - 10\,\mu$m diameter, distributed in hundreds of towsand on both surfaces. Fine particles can be inglobated in the stomata and the elements contained in the particle enter the leaf metabolism; a classical example of this being lead.

From an analytical point of view it is important to remark that the leaf itself can contribute peaks to the detected PIXE spectra. The penetration depth of 3 MeV protons into a leaf of average gross composition: 49% Carbon, 9% Nitrogen, 42% Oxygen[4], is about 130 μm. This thickness corresponds roughly to penetration into the epidermis of the leaf ($\approx 20\mu$m) and into the mesophyll (its central part) characterized by palisade

and spongy cells whose chemical composition reflects in the X-ray spectra. The primary elements Carbon, Hydrogen and Oxygen are below the range of applicability of PIXE. Above the sensitivity of PIXE are elements like K, Na, Ca, Mg, Fe, Mn, P, S, Cl, Si that are basic constituents of such cells [4] in quantities extremely dependent on the species examined and not predictable *a priori*. Their contribution to the X-ray spectra must therefore be separated from the contribution of the deposited particulate. A possible solution to this problem would be to subtract the PIXE spectra obtained from unpolluted leaves of the same species, like fresh ones collected in remote areas or even better very old samples recovered from botanical archives; we are exploring both ways.

THE METHOD OF ANALYSIS

One year leaves have been collected from low lying (about 2 m) branches in ten spots all over the town of Genova in industrial, central and residential areas. They have been dried in air for a week and packed individually for transportation at the Wits-CSIR Schonland Research Centre in Johannesburg where a very versatile PIXE facility is installed[5] [6]. One of its peculiarities is to allow irradiation of organic samples in a helium atmosphere so to improve to a large extent heat convection from the exposed sample, with very little effect on the beam current and spot due to the small energy loss and multiple scattering of protons in the thin layer of gas interposed ($\approx$ 1.5cm) between the protons entrance window (a thin mylar foil at the end of a nose extending into the PIXE chamber) and the sample. The same is true for the emitted X-rays that travel a couple of centimeters before entering the berillium window of the 100 mm^2, 5 mm thick Si(Li) detector positioned at 135 degrees to the beam direction. Helium pressure was kept slightly above atmospheric, but occasional admixture with air was observed from the presence of the Ar K_α peak in the spectra. Leaves were cut in 2 cm disks and glued to the standard impactor rings to be mounted, six at the time, on the remotely controlled sample weel which is a standard of the Wits PIXE chamber. Two sets of impactor rings were prepared to allow both the upper and the lower part of a leaf to face the proton beam without handling the weel. A funny filter consisting of two layers of kapton 500H (thickness= 5/1000") with a 5% hole was used. Standards were run in the same conditions for eventual calibration. Count rates from 700 to 1700 counts/sec were obtained using beam currents in the range from 5 to 15 nA with very low pile-up. Doses of 6 or 12 μC were accumulated. Beam spots of 6 mm diameter were sharply defined by the double changeable collimator associated to the chamber. A review of our work is given in Table I. Identified elements are listed in Table II

for all samples and compared to those present in an urban aerosol collected and analyzed with a different experimental equipment[7][8]. Three PIXE spectra from an industrial and densely inhabited area (Sample 9), from a central area characterized by heavy vehicular traffic (Sample 3) and from a park next to a residential area (Sample 2) are reported in figure 4. The effect of removing the surface deposition by careful washing of the leaf is seen in the two spectra of figure 5.

DISCUSSION

The spectra deconvolution analysis to determine the presence of elements in terms of physical quantities like [ng cm^{-2} time^{-1}], that are rather adequate to allow clear comparison of particulates concentrations in different area, is still in progress. It requires carefull subtraction of the leaf constituents contribution, but in principle, the quantity of material deposited per unit area can be determined with the precision allowed by comparison with standard targets (5%) and by the sharp definition (within 3%) of the beam area spun by the collimators. Only the particulate deposition time is affected by large uncertanties (15-20%, 2-3 months on a year). At present a few but relevant observations can be draw from our data.

First of all the characterization of urban aerosols from the PIXE spectra of leaves is as complete as that obtained from samples collected with specific devices (reference [7] and table II). This supports the adequacy of our method for the scope of elements identification. Also for those elements (like Vanadium) that cannot be identified *de visu* in our spectra, since swamped by higher intensity peaks, the deconvolution should give quantitative results.

Secondly the comparison of spectra in figure 5 shows clearly that elements like S, K, Ca, Ni, Zn, which are peculiar to the leaf or belong to the fine component ($< 1\,\mu$m) of the aerosol or both, are to a large extent accumulated below the surface[9]. Other, like Al, Si, Ti, Cr, Fe, are strongly reduced by washing as one would expect since they belong to the coarse part of the aerosol (Fe $5\,\mu$m, Ti $5\,\mu$m).

Thirdly some of the aerosol components that are known to be carried by particles in the fine stage[9] (Pb $0.5\,\mu$m, Mn $1.3\,\mu$m). are mostly incorporated by the leaf through its methabolism since they persist in the PIXE spectra even after the surface is deeply washed.

Fourthly the microscope analysis of the surface has revealed that the leaf acts as a filter for particles in a large range of diameters and seems to include those below $2.5\,\mu$m

that are more relevant to health problems. The numerical analysis will give strenght to the overall picture both in terms of a more precise definition of the effectiveness of our "sampler" and in terms of a comparison of different areas regards to single elements.

In conclusion, there is consistent support to the possibility of a large scale scan of pollutants dispersed in aerosol form over a wide urban area, that requires a simple approach. The experimental technique, that we have described in detail, including sample preparation and exposure to the proton beam, is relatively simple and can be easily implemented at any PIXE facility. Although this technique cannot supply absolute concentrations, we foresee however its great utility when exploited in parallel with the deployement of a small number of instrumental sampling stations in town, offering the possibility of large scale, inexpensive controls of the yearly or progressive (monthly) accumulation of pollutants aside prescribed sampling.

It is significant that our exploratory investigation took place in Genova, where press campaings on the high degree of pollution in the athmospfere are becoming quite sharp, and the demand for routine controls of the level of polllution is constantly increasing. This report gives some clue on a possible alternative way of considering, amongst the other pollutants, the also critical problem of particulates concentration that are reported[10] to be at the level of $144\,\mu g/m^3$ downtown and at $113\,\mu g/m^3$ in the suburbs.

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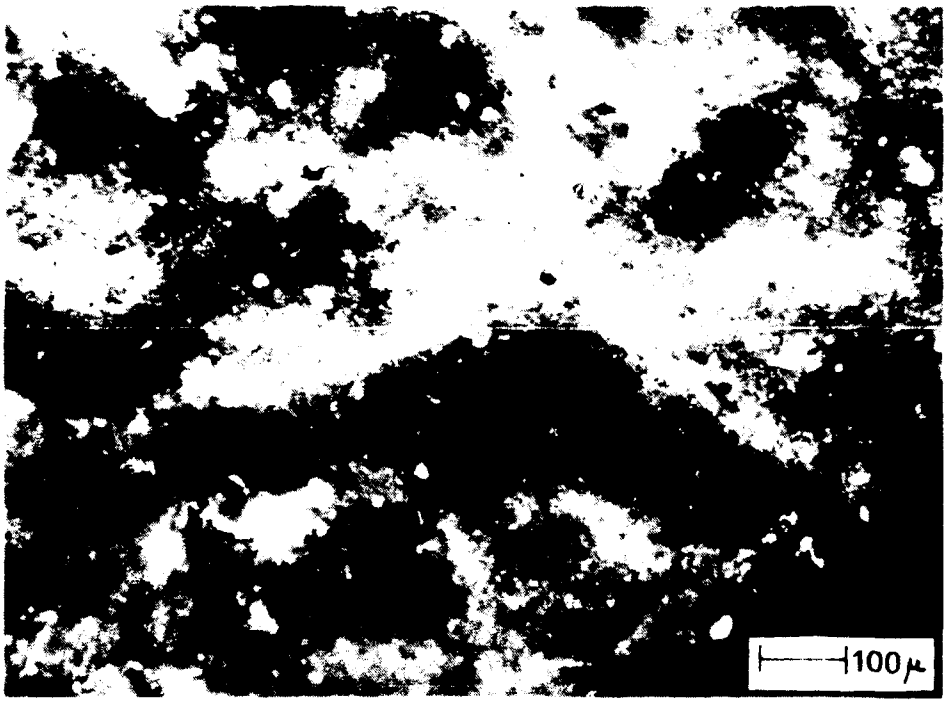

FIGURE 1 The upper (sample 8) surface of a leaf collected in the industrial and highly inhabited area of Cornigliano, as it is seen enlarged 32 times by a Zeiss-Axyomat microscope.

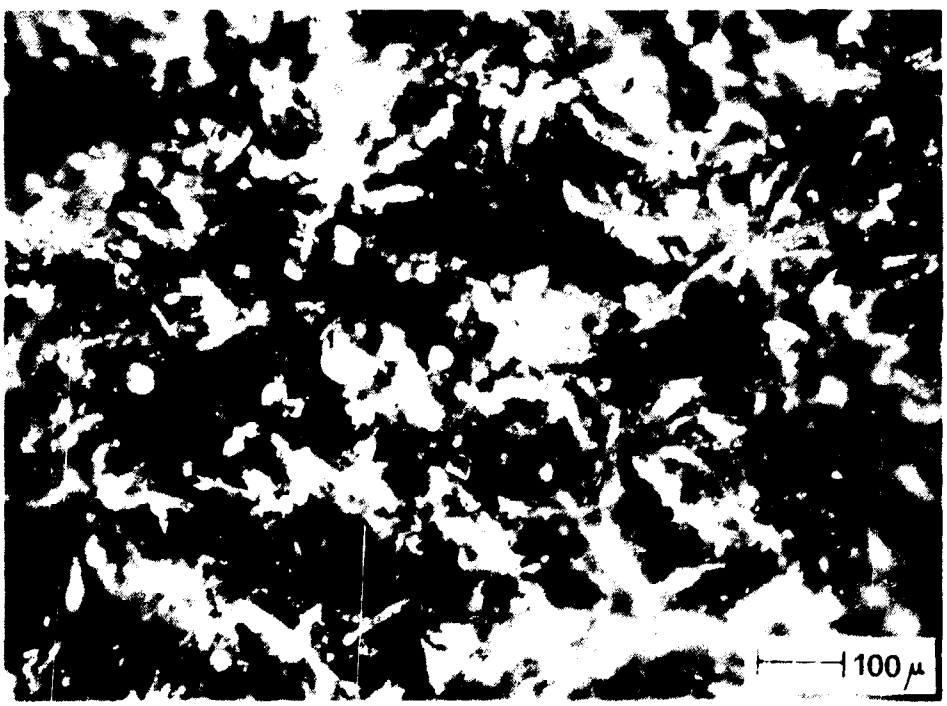

FIGURE 2 The lower (sample 9) surface of a leaf collected in the industrial and highly inhabited area of Cornigliano, as it is seen enlarged 32 times by a Zeiss-Axyomat microscope.

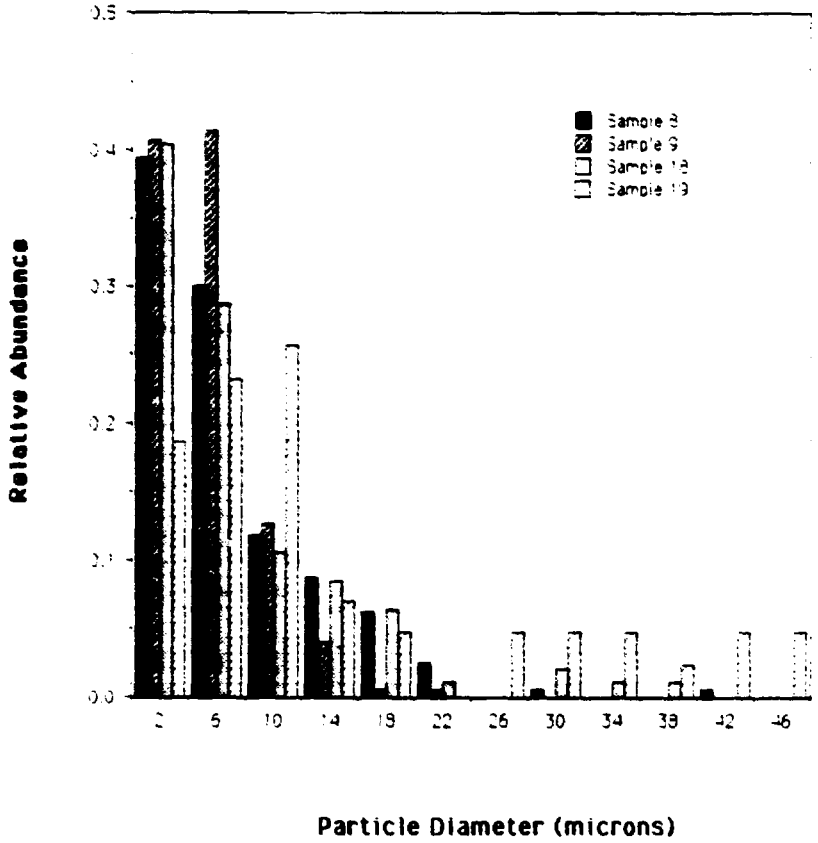

FIGURE 3 A classification of particles according to their diameter concerning samples 8, 9, 18 and 19 (see Table I for details).

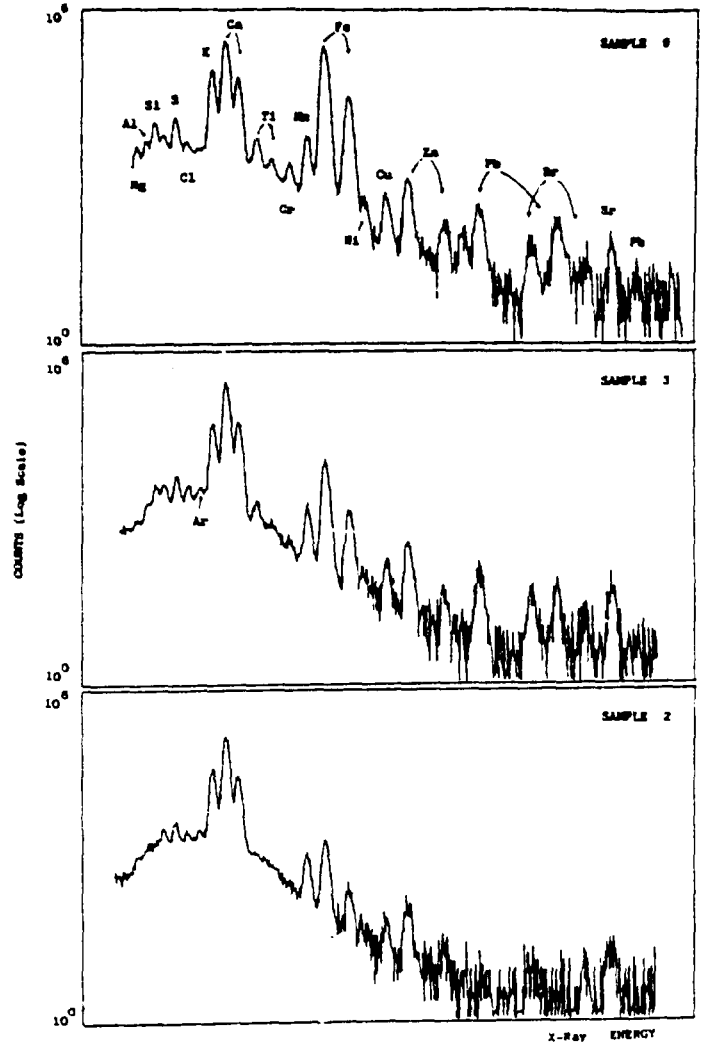

FIGURE 4 PIXE spectra from an industrial and densely inhabited area (Part a,Sample 9), from a central area characterized by heavy vehicular traffic (Part b,Sample 3) and from a park next to a residential area (Part c,Sample 2).

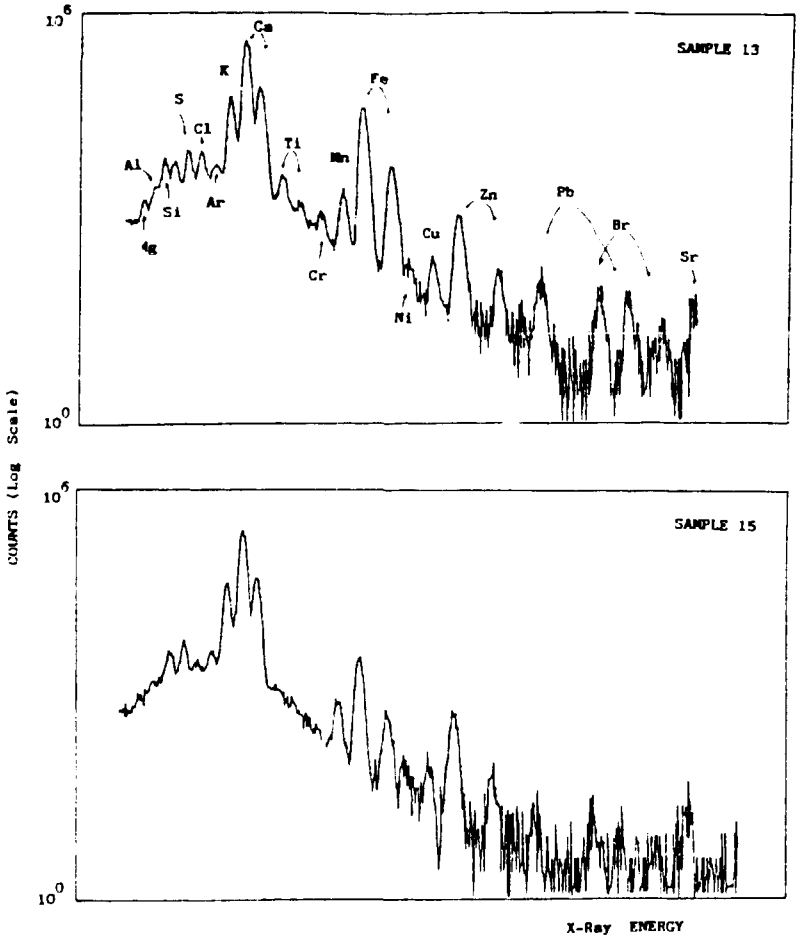

FIGURE 5 The effect of removing the surface deposition by careful washing of the leaf is seen from the comparison of the two spectra: raw (spectrum 13) and washed (spectrum 15).

TABLE I

SUMMARY OF PIXE SAMPLING AND EXPERIMENTAL CONDITIONS

Sample	Place of collection	Area	Leaf Side	Current [nA]	Count Rate [Hz]	Dose [microC]	Notes
1	GE–Quinto P.le Rusca	Residential	Upper	10	1000	6	
2	GE–Nervi Parco Serra	"	"	11	850	6	
3	GE Largo XII Ottobre	Central	"	10	1500	6	
4	GE Stazione Principe	"	"	11	900	6	
5	GE–SPD via Cantore	Industrial	"	12	1400	6	
6	"	"	Lower	12	1000	6	
7	"	"	"	15	1300	8	Another spot
8	GE–Cor. P.za Comune	"	Upper	5	1100	9	
9	"	"	Lower	13	1700	12	
10	GE–Pra P.za Bignoni	Residential	Upper	16	700	6	
11	"	"	Lower	16	700	6	
12	GE–Sestri via Soliman	Industrial	Upper	10	1400	12	
13	"	"	Lower	14	1500	12	
14	"	"	Upper	10	1000	8	Leaf washed
15	"	"	Lower	10	1200	6	"
16	GE P.za Terralba	Central	Upper	15	1000	12	
17	"	"	Lower	15	1500	12	
18	GE v.le Benedetto XV	"	Upper	10	1500	12	
19	"	"	Lower	15	1300	12	
20	Chamber Background			12	100	2.4	

TABLE II

SUMMARY OF ELEMENT DETECTION IN THE PIXE ANALYSIS OF LEAVES

Sample (•)	Na	Mg	Al	Si	S	Cl	Ar	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Br	Sr
1	N	N									N									
2	N	N	N	N						N	N	N			N			N		
3	N										N									
4	N	N									N									
5	N										N				N					
6	N	N									N									
7	N	N	N								N									
8	N										N									
9	N						N				N									
10	N						N				N									
11	N									N	N	N								N
12	N						N				N									
13	N										N									
14	N			N						N	N	N								
15	N	N	N	N						N	N	N								
16	N	N									N									
17	N										N									
18	N										N									
19	N	N									N									
20	N	N	N		N	N		N	N	N	N	N	N		N			N	N	N
Ref[7]							N													

N = Not evident in our PIXE spectra
(•) Sample numbers correspond to those of TABLE I