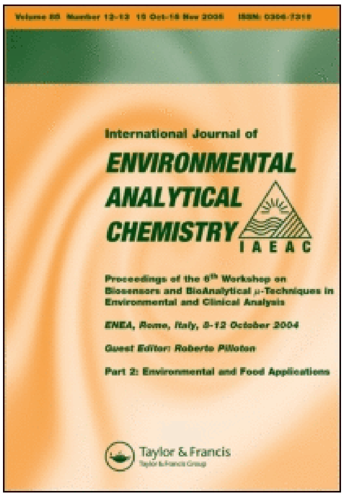

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RAPID MULTIELEMENT ANALYSIS OF TREE BARK BY EDXRF

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A rapid and simple method for multielement analysis of tree bark using energy dispersive X-ray fluorescence (EDXRF) spectrometry has been developed. Sample preparation consisted of crushing tree bark into a fine powder prior to the production of pressed pellets. Limits of detection for elements of interest (Pb, Hg, Zn, Cu, Ni, Al, Sn, Fe, Cr, Mn, Ti, As, Cd, Sb, and Ag) were at or below the µg/g level. Analysis of environmental certified reference materials (fly-ash, soil and tea-leaves) was used to check accuracy and precision. Survey analysis was performed at industrial, urban and rural sites in diverse locations throughout the world. The potential for source apportionation was demonstrated as reflected in elevated levels of Pb (up to 12,300 µg/g) and Sb (up to 86 µg/g) near a lead smelter site (UK) and high concentrations of Hg (up to 4.2 µg/g) in gold extraction regions of Brazil.

Keywords: Tree bark; EDXRF spectrometry; Multielement analysis; Source apportionation

INTRODUCTION

Tree bark has long been recognised as an effective passive sampler and bio-accumulator of airborne pollution, particularly for heavy metals in the environment [1]. Bark acts as the protective skin of the tree, guarding against, yet at the same time accumulating airborne material. Whilst some species have a relatively smooth, simply structured bark, others can exhibit a complex irregular structure, which may consist of layers of differing age. It is difficult to find the same species of tree with a similar type of bark in diverse geographical locations. Thus, it is almost impossible to develop a standardised sampling strategy. Accumulation of atmospheric aerosol and airborne particulate matter occurs through dry and wet deposition. Suspended particles may be retained following collision with the bark by impaction [2]. Retention of suspended particles is promoted by a moist, rough, or electrically charged surface [3] making bark a highly efficient collector. Particles or dissolved species may also be deposited on bark from rainwater although the influence of this process is less clear. Rain may fall directly on the bark or run down the trunk following collection in the crown.

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In addition, nutrient elements absorbed by trees from the soil or leaves could be transported to the bark [4], but this contribution is considered to be insignificant.

The majority of early studies to measure trace elements in tree bark have involved the determination of Pb from vehicular emissions in roadside trees. A number of studies have also been performed in areas affected by metal industries. Particularly high concentrations of Zn and Pb in bark were recorded near a smelter in the UK by Little [5]. Symeonides [6] presented similar but limited data for Cu, Zn, Cd and Pb near a smelter in Sweden. A study by Ward *et al.* [7] monitored emissions from a silver mine and treatment plant. In Finland, high Cu and Ni levels were reported by Poikolainan [8] near to a nickel refinery. Kakalu [9] reported elevated concentrations of Cd, Cu, Pb, Mn, Fe, Ni and Zn in a Nigerian study. Bohm *et al.* [10] determined heavy-metal concentrations in tree bark from industrialised areas of the Czech Republic. Most recently, Bellis *et al.* [11,12] reported on the use of tree bark and ICP mass spectrometry for the elemental and isotopic analysis of airborne derived uranium.

Most tree bark studies have been based on atomic absorption or ICP spectrometry, but there is considerable scope for the use of energy dispersive X-ray fluorescence (EDXRF) given its multielement capability and simplified sample preparation requirements. Bohm *et al.* [10] used X-ray fluorescence (XRF) to determine sulphur in tree bark as part of an environmental survey of the Czech Republic. In a related work, Selin *et al.* [13] reported on the multielement analysis of tree rings by EDXRF whilst the accumulation of elements in the annual rings of pine trees near a copper–nickel smelter was investigated by Larsson *et al.* [14].

In this study, tree-bark surveys were conducted in Sheffield, an industrial city in the north of England, and in various sites in Brazil. Further samples were collected from trees in London, Scotland, the Netherlands, France, Senegal and Malaysia, to enable comparison with Sheffield and give an overview of environmental contamination in respective countries. Bark samples were taken from areas of heavy industrial activity, busy city centers and remote areas.

EXPERIMENTAL

Sample Collection

The nature of the bark determined the sampling procedure. Rough, peeling bark was torn from the tree manually. Smooth, solid bark was removed using a sharp knife or a hammer and chisel and the material was stored in sealed brown paper envelopes. Plastic gloves were worn to avoid contamination. Comparison between samples collected manually and by knife or chisel from the same tree suggested that insignificant contamination is transferred from the sampling implement compared to the amount present in a sample. Approximately 100 g of external outer bark was removed from the target tree at a chest height of 0.5–1.5 m from the ground. Common beech (*Fagus sylvatica*) and Sycamore (*Acer pseudoplatanus*) were the usual species of tree sampled in England and Northern Europe. The absence of such species in other parts of the world meant that alternative ones had to be selected. For example, in Brazil, Sibipiruna (*Caesalpinea peltophorides*) and Mango (*Mangifera indica*) were sampled.

Sample Preparation

The bark sample was rapidly frozen by immersion in liquid nitrogen to render it brittle and immediately broken into small pieces by a fly-press. It was then crushed into a fine powder using a Tema-mill. The bark powder was then passed through a sieve (0.5 mm mesh) to remove any residual lumps. Between every sample, all equipment was carefully cleaned to prevent cross-contamination. Tree bark powder (4.0 g) was thoroughly mixed with 0.9 g of polystyrene co-polymer binder (Hoechst Wax, Spectro Analytical, U.K.) and pressed (12 tons load) to produce powder pellets for EDXRF analysis. Selected powder pellets were subjected to spiking to check on accuracy in the case of Hg determination. Prior to pressing, 4.0 g of tree bark powder was mixed with 2, 2.8, and 4 ml of Hg standard solution (10 mg/l) in acetone to give spikes of 5, 7 and 10 mg Hg/kg bark, respectively. The acetone was allowed to evaporate, leaving the bark powder coated with the desired spike of Hg. The dried powder was then pressed into a pellet in the normal way.

EDXRF Analysis

The powder pellets were analysed by EDXRF (X-LAB, Spectro Analytical, UK), the instrument having been pre-calibrated for 43 elements using a wide range of standard samples. To verify accuracy and precision certified reference materials (CRMs) were prepared and analysed using the same method as described above. The CRMs used were fly-ash (BCR 176), soil (SO-4) and tea-leaves (NIES-7). Artificially enriched pellets were also analysed to check the validity of the method for Hg.

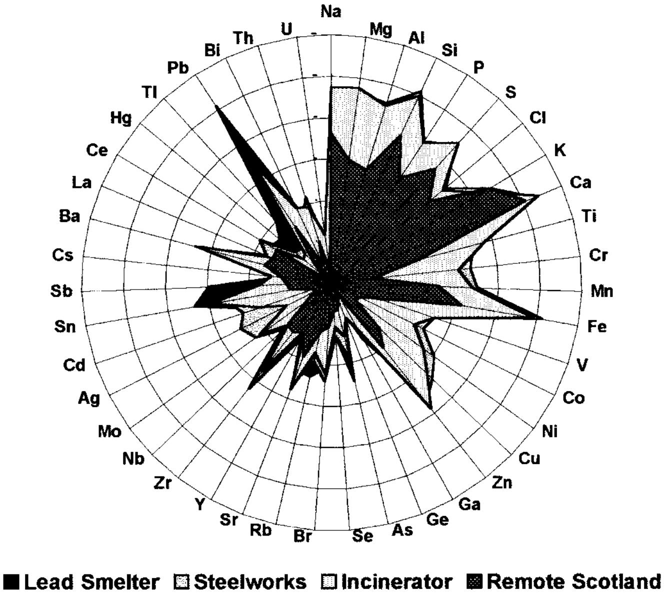
RESULTS AND DISCUSSION

A selection of results for the EDXRF analysis of tree bark for 15 elements is shown in Table I. In total, 98 bark samples from diverse locations around the world were analysed for 43 elements. Only a cross section of the most interesting results is presented here together with the range, mean, and median values to illustrate the high variability of the data. Despite the inconsistency of sampling and the standardisation difficulties associated with the use of tree bark as a bio-monitor [15], distinct trends and differences could be seen between the sample locations. Point source contamination by Pb, Al, Zn, Hg, Cd, As, Sb, Sn, and Ag were noted in and around the city of Sheffield. The high concentration values (see Table I) are consistent with industrial activity. The radial plot shown in Fig. 1 illustrates the contrasting concentrations of all 43 elements measured among three industrial sites in the UK and a relatively remote region in the North of Scotland. A radial plot depicting the variation in Fe, Al, Zn, and Pb concentrations in and around Sheffield is shown in Fig. 2. These plots help to visualise areas and sources of relatively high contamination. In particular, elevated concentrations of Pb (up to 12300 μg/g), Sb (up to 86.1 μg/g), As (up to 28.6 μg/g) and other heavy metals were found near a lead smelting works at Darley Dale (North Derbyshire, UK). For non-UK sites, the presence of Hg (4.2 μg/g), used for gold extraction in the central and wetland regions of Brazil, was confirmed. High levels of Al (7623 μg/g) and Sn (56 μg/g) were recorded for Malaysian and Senegalese samples probably as the result of unregulated waste incineration. With respect to Pb content, contrasts could be

TABLE I Analysis of tree bark

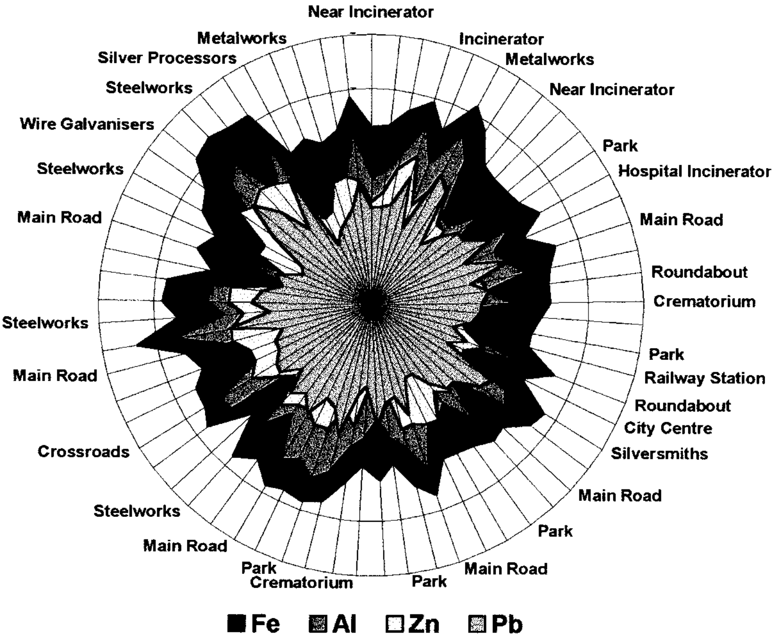
Location	*Pb* µg/g	*Hg* µg/g	*Zn* µg/g	*Cu* µg/g	*Ni* µg/g	*Al* µg/g	*Sn* µg/g	*Fe* µg/g	*Cr* µg/g	*Mn* µg/g	*Ti* µg/g	*As* µg/g	*Cd* µg/g	*Sb* µg/g	*Ag* µg/g
Sheffield, UK															
Isolated city park	18	< 0.5	35	17	6	38	3	967	10	78	37	0.6	0.3	1.2	< 0.5
Wire galvanisers	151	< 0.5	955	45	35	331	8	4868	117	137	194	1.8	2.3	1.2	< 0.5
Busy roundabout	157	< 0.5	137	54	12	132	4	1959	24	331	75	1.0	0.3	1.3	< 0.5
Metalworks	228	1.0	875	101	103	4010	30	18680	506	724	500	4.2	1.1	3.1	0.7
Incinerator	284	0.5	711	145	52	2329	70	8014	130	230	646	1.0	7.0	5.9	1.6
Silversmiths	420	1.2	87	112	16	1373	27	6067	50	78	164	6.3	0.5	2.4	2.2
Busy main road	433	0.5	60	67	7	438	5	3570	31	56	92	1.6	0.3	1.7	< 0.5
Steelworks	449	2.6	398	159	191	4911	30	21930	413	383	519	6.3	3.0	4.9	5.5
Non-ferrous metalworks	515	0.5	311	189	65	3232	30	13850	229	271	357	4.0	3.8	3.4	8.0
Silver processing works	590	1.4	497	226	106	3464	35	13890	226	314	340	7.5	17.9	2.8	29.2
Darley Dale, UK															
Lead smelting works	12300	4.1	90	101	21	300	217	3588	8	10	61	29	9.1	86.1	0.8
London, UK															
Buckingham Palace	14	1.6	41	16	3	131	1	862	4	39	38	0.5	< 0.3	0.8	< 0.5
Kings Cross	52	1.1	168	57	5	491	6	2037	8	31	106	0.9	< 0.3	1.7	< 0.5
Invergarry, Scotland															
Caledonian canal forest	4	< 0.5	10	4	1	71	1	147	1	38	15	0.5	0.3	1.2	< 0.5
Nice, France															
Pedestrianised precinct	7	0.5	21	10	1	234	< 0.6	233	1	12	28	0.4	< 0.3	0.6	< 0.5
Busy promenade road	50	< 0.5	45	18	2	194	3	459	5	4	33	0.8	< 0.3	1.2	< 0.5
Amsterdam, Holland															
Museum forecourt	13	< 0.5	27	11	3	69	1	528	5	39	35	0.5	< 0.3	0.5	< 0.5
Busy main road	21	0.5	69	32	7	388	2	1488	6	48	69	0.6	< 0.3	0.8	< 0.5

Ipoh, Malaysia															
City centre park	10	< 0.5	33	5	2	4703	23	842	5	31	217	0.4	< 0.3	< 0.3	< 0.5
Busy main road	26	0.5	73	29	3	7623	56	2274	5	42	197	2.1	< 0.3	1.2	< 0.5
Dakar, Senegal															
School compound	9	0.5	7	5	2	401	1	410	5	9	32	0.4	< 0.3	1.2	< 0.5
Busy main road	20	0.5	15	11	2	1700	3	1443	5	11	76	0.6	< 0.3	< 0.3	< 0.5
Brazil															
Nobres, Savannah land	1	1.0	4	5	2	71	1	240	5	7	19	0.2	< 0.3	0.1	0.1
Sorrizo, Amazon rain forest	1	0.5	2	5	1	297	1	598	5	16	30	0.2	< 0.3	1.2	0.1
Pocone, gold mining town	5	4.2	13	7	2	2063	1	3258	5	130	119	0.3	< 0.3	0.1	0.3
Cubatao, industrial city	11	1.1	171	27	9	3051	2	5109	11	230	294	0.5	0.8	0.2	0.1
Sao Paulo, busy city center	20	0.9	118	25	5	554	1	571	4	22	63	0.6	< 0.3	0.5	0.1
EDXRF-Limits of Detection	0.2	0.5	0.2	0.4	0.6	5.0	0.6	0.8	0.8	0.8	0.8	0.2	0.3	0.3	0.5
(Statistics for 98 Bark samples)															
Min. Concentration	0.6	< 0.5	2	4.7	0.8	34	< 0.6	233	< 0.8	3.8	15	0.2	< 0.3	< 0.3	< 0.5
Max. Concentration	12300	4.2	955	226	275	7623	217	21930	506	7752	618	28.6	17.9	86.1	29.2
Concentration Range	12299	3.9	953	221	274	7589	216	21698	505	7748	599	28.4	17.8	86	29.1
Mean	259	0.73	181	49	25	956	16	3659	59	217	146	1.7	1.1	2.3	1
Median	71	0.5	119	32	13	433	8	2135	31	96	107	0.8	0.4	1.2	0.5



Concentration Range 0–100,000 μg/g

FIGURE 1 Contrasting elemental concentrations at three Industrial sites and comparison with a remote area of Scotland.



Concentration Range 0–100,000 μg/g

FIGURE 2 Contrasting concentrations for Fe, Al, Zn, and Pb in and around Sheffield.

TABLE II Analysis of certified reference materials

	Pb µg/g	*Hg* µg/g	*Zn* µg/g	*Cu* µg/g	*Ni* µg/g	*Al* µg/g	*Sn* µg/g	*Fe* µg/g	*Cr* µg/g	*Mn* µg/g	*Ti* µg/g	*As* µg/g	*Cd* µg/g	*Sb* µg/g	*Ag* µg/g
BCR176 (fly-ash)	10770	28.2	22420	1301	130.8	99640	5308	21560	548.5	783.2	8921	73.2	505.1	372.1	79.2
certified values	10870	31	23770	1302	124	101500	5900	21260	663	1099	8510	93	470	412	–
SO-4 (soil)	16.4	10.5	92.4	23.8	23.8	68130	1.3	23810	67.6	696.4	3837	5.5	1	1.2	< 0.5
certified values	14	< 0.5	94	21	24	64095	2	23570	64	620	3477	7	< 0.3	0.7	< 0.5
NIES- 7(tea leaves)	1.9	< 0.5	40.1	9	7.8	4400	1.2	164.5	0.6	611.3	34.1	0.2	< 0.3	1.2	< 0.5
certified values	1	–	33	7	7	4555	–	–	< 0.8	700	–	–	< 0.3	< 0.3	–

TABLE III Precision data for tree bark powder pellets (Sheffield)

	Pb µg/g	*Hg* µg/g	*Zn* µg/g	*Cu* µg/g	*Ni* µg/g	*Al* µg/g	*Sn* µg/g	*Fe* µg/g	*Cr* µg/g	*Mn* µg/g	*Ti* µg/g	*As* µg/g	*Cd* µg/g	*Sb* µg/g	*Ag* µg/g
A2A	116	11.2	182	67	20	168	32	4171	48	105	118	2.0	0.8	1.2	0.7
A2B	114	5.2	187	68	18	106	30	3720	42	97	98	1.3	0.8	1.2	0.7
A2C	121	9.3	195	69	20	125	29	4011	49	112	127	2.6	0.9	1.1	0.7
mean	117	8.6	188	68	19	133	31	3967	46	105	114	2.0	0.8	1.2	0.7
SD	4	3.1	6	1	1	32	1	229	4	8	15	0.7	0.1	0.1	0.0
% rad	3	36	3	1	7	24	5	6	8	7	13	33	7	5	0
X1A	50	12.3	595	57	213	2998	4	11730	17	5717	147	4.6	6.0	1.1	0.4
X1B	55	6.0	634	59	234	2798	4	12570	16	6339	161	3.9	6.4	0.9	< 0.1
X1C	59	9.4	683	65	246	3036	4	14220	16	6995	218	4.2	7.0	1.3	0.6
X1X	62	1.3	726	66	270	3750	4	14880	16	8031	195	5.7	6.9	0.9	0.5
mean	57	7.3	659	62	241	3146	4	13350	16	6771	180	4.6	6.6	1.1	0.5
SD	5	4.7	57	4	24	416	0	1453	0	989	32	0.8	0.5	0.2	0.1
%rsd	9	65	9	7	10	13	2	11	1	15	18	17	7	18	20

TABLE IV Hg spike recoveries for tree powder pellets

Sample	*Spike* µg/g	*Hg* µg/g	*% Recovery*
A2	no spike	0.5	–
A2a	5	5.2	94
A2b	7	9.3	126
A2c	10	11.2	107
X1	no spike	1.3	–
X1a	5	6.0	94
X1b	7	9.4	116
X1c	10	12.3	110
X8	no spike	0.8	–
X8B	5	7.0	124
X8C	7	8.4	109
X8A	10	13.0	122

seen for all major cities between busy main roads and minor roads reflecting contributions from leaded gasoline.

Regarding the standardisation of sampling there is a difficulty since the same species of tree cannot be found at all the sampling locations. However, within the context of survey analysis, the results of Table II together with the precision data of Table III indicate that the developed methodology is fit for the purpose. Given the extreme and indiscriminate use of Hg for gold extraction in parts of Brazil the presence of Hg in tree bark at the ppm level (4.2 µg/g) is a most interesting finding. The spike recovery results shown in Table IV indicate a reliable method for this element.

CONCLUSIONS

EDXRF has been shown to provide a useful new approach for multielement analysis of tree bark. The results of survey analysis show the clear potential for source apportionation. Future work will investigate what effect, if any, seasonal variations of temperature and rainfall have on the results. Whilst the method can be considered to be rapid in terms of sample preparation and analysis time, a considerable amount of time is spent on collection and travel between the laboratory and sites. We plan to investigate alternative methods using portable or hand-held XRF Spectrometers for *in-situ*/field measurements [15] and conduct extensive tree bark surveys in specific areas enabling production of elemental maps similar to those produced by geochemical surveys using soil samples.

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