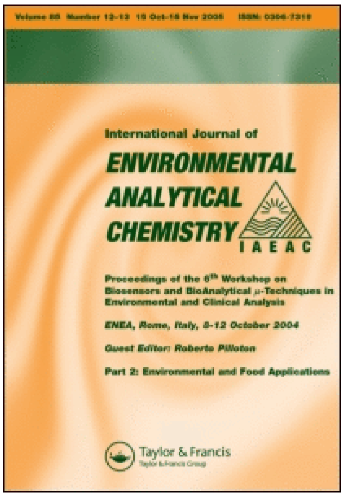

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Quantitative Surface Analysis of NBS Standard Materials and Mt. St. Helens Ash by Electron Spectroscopy for Chemical Analysis†

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Results are presented which develop a quantitative method of surface analysis by ESCA for complex heterogeneous systems. Calibration and application of the method to determination of surface weight percentages are discussed. Mt. St. Helens Ash is used to authenticate the method; results agree with bulk analysis to ±20%. Results from NBS standard materials are used to establish detection limits of 0.1% by weight for most materials. The minimum detectable concentration of surface segregated species can be as low as 200–300 ppm. Results from the NBS standards establish a surface composition for these species, and allow deduction about particle morphology; organics and volatile metals are likely to be surface segregated and mineral species are segregated to the particle core.

KEY WORDS: ESCA, surface analysis, particle morphology, NBS standard materials, Mt. St. Helens, ash.

INTRODUCTION

The application of modern surface spectroscopic methods, such as X-Ray Photoelectron Spectroscopy (XPS or ESCA), Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS) and Ion Scattering Spectroscopy (ISS), to the analysis of complex heterogeneous samples has been limited by the lack of rigorous quantitative data derivable from these methods.[1] While each method yields important data regarding qualitative surface composition and changes in concentration which occur at surfaces,

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successful interpretation of spectral intensity data as surface concentration values is difficult for heterogeneous systems.[1,2] Many methods are available for converting ESCA ,[3-6] AES,[7] and SIMS[8] peak intensities to surface concentrations, based both on empirical "sensitivity factors" and on evaluation of fundamental parameters. These techniques have been most successful when applied to systems of simple composition. Some attempts have been made to utilize empirical methods for converting ESCA intensities for "semi-quantitative" analysis of complex heterogenous surfaces, such as coal and fly ash,[9] Mt. St. Helens Ash (MSHA),[10] geological samples[11] and catalysts.[12] These results were limited in that minimum detectable concentrations were only ca. 2%, probably due to the instrumental factors.

The present study focuses on environmental particle samples as examples of complex heterogeneous surfaces, which are used to develop and test a quantitative method of ESCA analysis, and to determine minimum detectable concentrations, both at the surface and in the bulk. ESCA was chosen over AES and SIMS because previous studies[13-15] have been limited to qualitative analysis and depth profiling of large single particles, with charging effects and sample destruction by electron (AES) or ion (SIMS) beams complicating quantitation.[16]

The present study presents data from ESCA analysis of Mt. St. Helens Ash (MSHA) and NBS Standard Reference Materials (SRM) 1648, Urban Particulate Matter and 1633a Coal Fly Ash. The data are analyzed using both fundamental and experimental parameters to convert peak intensities to surface weight percentages. The method is calibrated with MSHA, a sample shown previously to exhibit very little surface/bulk heterogeneity.[10,17,19] The same method is used to correct ESCA data from both SRM's, providing minimum detection limits from ESCA analysis, and surface compositional data for the SRM's which can be used as a reference for further work on heterogenous samples.

Experimental

ESCA spectra were recorded on an AEI ES200A electron spectrometer fitted with a DS100 data system. The data system is interfaced to an interactive Apple II Plus (48K) microcomputer with a Corvus Winchester Disk for data storage and processing. Peak areas from integrated intensities were calculated with this system. The AEI ES200A was operated at a base pressure below 10^{-8} torr, during analysis. Al Kα radiation (1486.8 eV) at 12 kV and 22 mA was used as the excitation source. Width of the Au $4f_{7/2}$ line under operating conditions was 1.2 eV.

All binding energies were calibrated to an internal standard of the carbon 1s line at 284.6 eV for MSHA and SRM 1633a, and 285.0 eV for

SRM 1648, referenced to vacuum deposited gold; Au $4f_{7/2}$ line at 83.8 eV.[20] The difference in carbon 1s lines is attributed to the different types of carbon which are dominant on each sample. Both MSHA and SRM 1633a exhibit a significant low binding energy carbon component (i.e. "free" or graphitic/pyrolytic carbon), while the carbon species in SRM 1648 is mostly organic, which correlates with the high content of adsorbed organic species known for this SRM.[21] Binding energies were compared to values for standards measured by the AEI ES200A, reported in Table I, and to published values.[22]

TABLE I

Selected ESCA reference binding energies and auger parameters

Element/ state	Photoelectron line	Binding energies (± 0.2 eV)	Auger parameter[23]	Reference compound
NH_4^+	1s	401.2	—	$(NH_4)_2SO_4$
NO_3^-	1s	407.4	—	$NaNO_3$
Si^{+4}	2p	103.1	—	SiO_2
Si^{+4}	2p	102.6	—	$CaSiO_3$
Al^{+3}	2p	74.5	—	Al_2O_3, $AlPO_4$
S^{+6}	2p	168.6	—	$(NH_4)_2SO_4$
Ca^{+2}	2p	346.6	—	CaO
Ca^{+2}	2p	346.9	—	$CaSiO_3$
Cl^-	2p	198.2	—	NaCl
Fe^0	$2p_{3/2}$	706.4	—	Fe
Fe^{+2}	$2p_{3/2}$	710.8	1409.7	$(NH_4)_2Fe(SO_4)_2$
Fe^{+3}	$2p_{3/2}$	710.6	1409.0	Fe_2O_3
K^+	$2p_{3/2}$	292.8	—	KCl
Na^+	1s	1071.9	1569.3	NaCl, $NaNO_3$
P^{+5}	2p	134.0	—	$AlPO_4$
Mg^{+2}	2p	50.0	—	$MgCl_2$
Co^{+3}	$2p_{3/2}$	779.8	—	Co_2O_3
Ba^{+2}	$3d_{5/2}$	780.5	—	$BaDl_2$

NBS standard reference materials were purchased from the Department of Commerce, and were stored in a dessicator over P_2O_5. Mt. St. Helens Ash (18 May 1980 blast) was collected from dry deposition at Keller Washington, and also stored over P_2O_5 in a dessicator. Samples were mounted on double sided tape for ESCA analysis.

Quantitative Calculations

The method for converting ESCA intensity ratios to atomic ratios was to use the following equation:[24]

$$\frac{N_x}{N_s}=\frac{I_x}{I_s}\frac{\sigma_s\lambda_s\phi_s}{\sigma_s\lambda_s\phi_s}\frac{T_sD_s}{T_xD_x} \tag{1}$$

The subscripts x and s represent values for the elements of interest and the internal standard, respectively. The variables are defined as:

N = number of atoms in the sample volume;
I = integrated ESCA peak intensity;
σ = atomic cross section for photoionization (1487 eV);[25]
λ = relative escape depth factor;[26,27]
ϕ = spectrometer photoelectron angular factor;[28]
T = transmission function of spectrometer;[29]
D = overlayer (contamination) attentuation.[24]

It is assumed that values for T and D cancel each other[24,29] since both ratios have been shown to be near unity. Relative escape depths are calculated assuming $\lambda \propto (\text{kinetic energy})^{0.67}$ since all kinetic energies measured are greater than 300 eV.[26] Cross sections are taken from the Schofield tabulation.[25] The spectrometer photoelectron angular factors are calculated as described[28] for the 90° angle between source and detector in the AEI ES200A spectrometer. Atomic ratios (N_x/N_s) are then converted to atomic percentages by Eq. 2. The value of unity in the denominator is added to the standard $(N_s/N_s = 1)$. Weight percentages are then calculated from atomic percentages.

$$\text{Atomic \% of species } x = \frac{(N_x/N_s)}{\left(1+\sum_i (N_x/N_s)\right)} \times 100 \tag{2}$$

Previous work[24] has used Eq. 1, but only for one element of interest, ratioed to the standard with known bulk concentration. Thus the present work is the first approach a complex heterogeneous system in this manner. The previous studies of MSHA[10] and NBS 1633(a)[9] by "semi-quantitative" ESCA analysis used a similar approach, however, previous authors did not consider many factors taken into account in this work. For example, the ϕ factor[27] was pointed out as not being important;[11,12] however, recent studies have shown the importance of this factor.[30] Besides observing lower detection limits, we believe the present quantitative treatment to be more valid than previous work,[9-12] and results more representative of the actual surface concentrations.

RESULTS AND DISCUSSION

A. Mt. St. Helens Ash (MSHA)

Qualititative and quantitative results from the ESCA analysis of Mt. St. Helens Ash (MSHA) are presented in Tables II and III. These data can be compared to the previously published bulk concentrations,[10,17–19] also listed in Table III. All reported bulk major constituents (>0.1% by weight) except titanium and manganese are detected. No trace constituents (<0.1% by weight) could be detected. Additionally, carbon and nitrogen were detected, probably present as hydrocarbons and amines. These elements have not been reported previously. The chemical states assigned are not surprising, in that they are all oxides (except carbon and nitrogen); bulk analysis assumes this state.[17–19] In fact, many of the elements are probably present not as simple oxides, but as complex mineral species. However, since the matrix cores of these particles vary from glassy to highly crystalline[18,19] it is not possible to infer a particular mineral structure from ESCA binding energies.

Previous bulk analyses have shown MSHA to be extremely homogeneous in composition.[17–19] Non-magnetic, explosive production

TABLE II

ESCA qualitative results for Mount St. Helen's Ash

Element	Photoelectron line	Binding energy[a]	Auger parameter[b]	Chemical state
Si	2p	102.8	—	Si^{+4}
Al	2p	74.5	—	Al^{+3}
Fe	$2p_{3/2}$	711.5	1411.3	Fe^{+3}
Ca	$2p_{3/2}$	348.5	—	Ca^{+2}
Na	1s	1072.3	1580.0	Na^{+}
Mg	2p	50.0	356.2	Mg^{+2}
K	$2p_{3/2}$	293.4	—	K^{+}
Cl	2p	n.d.[c]	—	—
Ti	2p, 2s	n.d.[c]	—	—
S	2p	n.d.[c]	—	—
P	2p	n.d.[c]	—	—
Mn	2p	n.d.[c]	—	—
N	1s	400.0	—	NH_x
C	1s	284.6	—	CH_x
O	1s	532.0	—	oxides

[a] (± 0.15 eV).

[b] Calculated as modified Auger parameter.[23]

[c] Not detected.

TABLE III

Quantitative surface analysis of Mt. St. Helen's ash comparison to bulk results

Element	Bulk %[17–19a,b]	Bulk %[c]	Surface % (±5%)[c,d]
Si	65.0±3.3	30.3	35.8
Al	16.9±0.7	9.0	9.7
Fe	4.81±1.1	3.4	4.3
Ca	4.94±0.17	3.5	0.9
Na	2.21±0.94	1.6	0.7
Mg	1.47±0.28	0.9	6.2
K	0.69±1.13	0.6	1
Ti	0.37±0.09	0.2	n.d.
Mn	0.56±0.16	0.4	n.d.
P	0.077±0.020	0.04	n.d.
S	0.0846±0.0380[c]	0.08	n.d.
Cl	0.0663±0.0182[c]	0.06	n.d.
C	not given	—	6.5
N	not given	—	0.2

[a] Taken as average of nine different ground stations.
[b] As the oxide.
[c] As the element.
[d] Calculated as in the text.

of MSHA would imply that the particles should have very little surface/bulk heterogeneity, i.e. the bulk composition should reflect the surface composition. Thus, MSHA is an ideal calibrant for the ESCA quantitation method proposed in this work and ESCA should yield concentration values which are equivalent to the bulk values within experimental error. Examination of data in Table III shows the quantitative method is accurate for the concentration values of the major constituents, to about 20%. This value is the often quoted limit for absolute quantitation of even single systems by ESCA,[2] so the analysis is quite successful, given the number of species and the complexity of the sample.

A closer examination of the quantitative results indicates some deviation from the simple surface/bulk equivalence picture. Calcium and sodium values fall below the bulk levels, while magnesium concentration is above the bulk value. There are two possible interpretations for this result; either the method fails for these species or there may be surface enrichment (Mg) and depletion (Ca, Na). Given the alkaline character of water extracts of MSH,[17–19] segregation of Mg at the surface would be expected, supporting the latter explanation.

These results point out one value of this ESCA method, assuming an accuracy of ±20%, for identifying species which are surface segregated (surface enriched in comparison to the bulk) or segregated in the bulk (surface depleted in comparison to the bulk). For particles where depth profiling by ion sputtering and AES and SIMS analysis is problematic because of small particle size[13-16] the ESCA method may be a preferable means of identifying surface species. Finally, the seemingly anomalous results of the previously undetected carbon and nitrogen may be explained by the analysis techniques used. Most likely these species are adsorbed, and the bulk techniques used previously (emission and X-ray fluorescence) are not sensitive for these elements.

B. Standard Reference Material NBS 1648

The method established has been used for study of the SRM's, where significant surface/bulk heterogeneity is expected.[21] For a valid surface quantitative method, species which are surface segregated will give surface concentration values enriched significantly compared to the bulk. Conversely, species segregated to the center of the particles will give values depleted when compared to the bulk.[16,31] Identification of the segregated species can be accomplished by comparing surface and bulk values in this manner. Such an analysis will provide reference data on surface composition of a well (bulk) characterized sample. Also the SRM's provide a system for specifying detection limits. One can define two types of detection limits, the surface detection limit, i.e. the minimum surface concentration that can be sensed, and the bulk detection limit, which is the minimum detectable concentration in the bulk that can be detected, most likely if the particular species is entirely surface segregated.[2]

Tables IV and V give the qualitative and quantitative results for NBS SRM 1648, Urban Particulate Matter. Fourteen elements were detected. They can be distinguished as organic, metals and inorganic (oxide) species. Of the organics, carbon is primarily hydrocarbon and nitrogen is detected both as amine and nitrate. Sulfur is primarily inorganic sulfate and chlorine is chloride. Of the metals, lead and zinc are most likely halides, sulfates or oxides. This result has been seen often for these volatile toxic elements on particle surfaces.[33,34] The mineral inorganic species, calcium, silicon, iron, aluminium, sodium, phosphorus, and magnesium are probably oxides or mineral species. Again, no complex mineral species can be postulated from the ESCA data alone.

Quantitative data in Table V[35,36] allow several conclusions to be drawn about particle structure and morphology. In general, species presumed to be adsorbed, i.e. organic and volatile toxic metals, are found to be surface

TABLE IV

ESCA qualitative results for NBS 1648 urban particulate matter

Element	Photoelectron line	Binding energy (± 0.15 eV)	Chemical state
C	1s	285.0	CH_x
		286.5	CO
N	1s	400.5	NH_x
		405.7[a]	NO_3^-
S	2p	169.2	SO_4^{-2}
Cl	2p	200.3	Cl^-
Pb	$4f_{7/2}$	139.3	PbX_2
Zn	$2p_{3/2}$	1023.2	ZnO or ZnX_2
Na	1s	1072.1	Na^+
P	2p	134.0	PO_4^{-3}
Mg	2p	50.0	MgO
Si	2p	103.0	SiO_x
Al	2p	74.8	AlO_x
Fe	$2p_{3/2}$	711.2	FeO_x
Ca	$2p_{3/3}$	348.8	CaO_x
O	1s	532.5	mineral oxides

[a] From LN_2 measurements.

enriched, values for the mineral species, assumed to the center of the particle, are depleted in comparison to the bulk. Specific results are quite illustrative of this general morphology. The most obvious and dramatic result is the value for carbon. The value for total carbon is enriched by a factor of four at the surface compared to the bulk value.[21] This lends credence of the assignment to adsorbed hydrocarbons. Other species which could be adsorbed are nitrogen, sulfur, lead and chlorine; all are enriched to varying degrees. Concentrations of the mineral elements, such as silicon, aluminum and iron are depleted at the surface. Overall, these quantitative results support a morphology of minerals as a core with adsorbed organics and volatile toxic metals, and some inorganics segregated at the surface. The results also establish a surface composition for the SRM. Results on detection limits indicate that species below 0.2% by weight were not detected for SRM 1648, including the variety of trace elements at the parts per million level, showing that none of these species is strongly surface segregated.

C. Standard Reference Material NBS 1633a

The qualitative and quantitative results for NBS SRM 1633a, Coal Fly

TABLE V

Comparison of bulk and surface composition for NBS 1648

Element	Bulk wt%[a,b]	Surface wt % (±5% r.s.d.)	Surface atomic % (±5% r.s.d.)
C	14.0	59.0	71.0
N	2.01[c]	3.8	3.9
S	5.14	5.5	3.9
Cl	0.45	0.88	0.40
Pb	0.655	1.2	0.90
Zn	0.48	0.15	0.30
Na	0.4	0.80	0.50
P	n.a.	1.5	0.72
Mg	0.8	0.60	0.36
Si	12.5	5.1	2.6
Al	3.3	1.9	1.00
Fe	3.91	0.55	0.15
Ca	n.a.	1.8	0.60
O	n.a.	17.3	15.6
Ti	0.4	n.d.	n.d.

n.a. = not available from NBS.

n.d. = not detected.

[a] In addition values for Cu (609 ppm), Cr (403 ppm), As (115 ppm), Cd (75 ppm), Ni (82 ppm), U (15.5 ppm) are certified, but undetectable by ESCA.

[b] In addition values for Sb (45 ppm), Ba (137 ppm), r (500 ppm), Ce (55 ppm), Cs (3 ppm), Eu (0.8 ppm), Hf (4.4 ppm), In (1.0 ppm), I (20 ppm) V (130 ppm), La (42 ppm), Sm (4.4 ppm), Sc (7 ppm), Se (24 ppm) Ag (6 ppm), Th (7.4 ppm) and W (4.8 ppm) are reported, but below ESCA detection limits.

[c] Ammonium N only.

Ash are given in Tables VI and VII, respectively. Thirteen species are detected, again designated as organic, metals and inorganics: specifically, carbon, nitrogen, phosphorus, sulfur, silicon, aluminum, iron, sodium, potassium, calcium, barium and magnesium. The chemical state results are interesting. The carbon line was very broad, with a significant low binding energy component. This results in the assignment of some "free" or graphitic/pyrolytic type carbon, besides the organic hydrocarbon species; nitrogen is totally amine-type nitrogen, and the sulfur is sulfate. The inorganic species are primarily oxides, with the metals likely present as oxides or sulfates. Overall, none of the chemical state results is surprising.

The quantitative results yield[36,37] some interesting conclusions. First, the mineral species, Al, Si, Fe, Na, K and Ca are all surface depleted or detected at equivalent surface/bulk levels. The organic and inorganic species, carbon, nitrogen, sulfur and phosphorus are all surface enriched. Neither result is too surprising given the assumption that organic material

TABLE VI

ESCA qualitative results for NBS 1633a coal fly ash

Element	Photoelectron line	Binding energy (± 0.2 eV)	Chemical state[16,20]
C	1s	284.6	CH_x, C(graph)
		286.8	CO
N	1s	400.0	NH_x
S	2p	169.6	SO_4^-
Ba	$3d_{5/2,3/2}$	780.7/795.7	Ba^{+2}
P	2p	134.1	PO_4^{-3}
Al	2p	75.0	AlO_x
Si	2p	103.0	SiO_x
Fe	$2p_{3/2,7/2}$	711.8/724.9	FeO_x
Na	1s	1071.9(2059.0)	Na^+
	(Auger parameter)[20]		
K	$2p_{3/2}$	292.8	K^+
Ca	$2p_{3/2,1/2}$	347.9/351.4	CaO_x
Mg	Auger, 2p	306.1, 50.0	MgO_x
O	1s	532.1	oxides

Au = LMM Auger line.

TABLE VII

Comparison of bulk and surface composition for NBS 1633a

Element	Bulk wt. %[36,37,a,b,c]	Surface wt.% ($\pm 5\%$ r.s.d.)	Surface atomic % ($\pm 5\%$ r.s.d.)
C	n.a.	26	39
N	n.a.	0.27	0.35
S	0.27	1.1	0.65
Ba	0.15	0.77	0.10
P	0.2	0.52	0.31
Al	14.0	13	8.6
Si	22.8	21.0	14.0
Fe	9.40	2.6	0.85
Na	0.17	0.08	0.06
K	1.88	1.8	0.85
Ca	1.11	0.98	0.44
Mg	0.455	1.4	1.0
O	n.a.	30.0	34.0
Ti	0.8	n.d.	n.d.

n.a. = not available.

n.d. = not detected by ESCA.

[a] Additionally, As (145 ppm), Cd (1 ppm), Co (46 ppm), Cs (11 ppm), Ea (4.ppm), Ga (58 ppm), Hf (7.6 ppm), Mn (190 ppm), Mo (29 ppm), Sb (7 ppm), Sc (40 ppm), V (300 ppm) are reported by NBS and below ESCA detection limits.

[b] Additionally, Be (12 ppm). Ce (180 ppm), Co (46 ppm), Cs (11 ppm), Eu (4 ppm), Ga (58 ppm), Hf (7.6 ppm), Mn (190 ppm), Mo (29 ppm), Sb (7 ppm), Sc (40 ppm), V (300 ppm) are reported by NBS and below ESCA detection limits.

[c] Additionally, Nd (65.6 ppm), Sm (16 ppm), Gd (15.3 ppm) (ref. (33)). are reported values and are below ESCA detection limits.

will be adsorbed, and thus surface segregated. Two interesting results are the enrichment of barium and magnesium, most likely present as adsorbed sulfates or halides.[38] These results indicate the enhanced detection limits of ESCA, when a species is surface enriched. This result will be discussed further in the following section. Again these results establish a surface composition for this SRM, along with developing a method of identifying surface species and species at the center of the particles.

D. Detection Limits

Results from all three analyses show that the minimum surface concentration detectable is no better than 0.1% by weight. However, this can be interpreted in two ways. First, if a species is significantly surface enriched, the minimum detectable bulk concentration may be much lower. This result is exemplified by the NBS SRM 1633a barium results, where the species present at 0.15% by weight in the bulk is enhanced by a factor of 5 at the surface (0.77% surface weight percentage). Thus, if the surface detection limit of 0.1% by weight is for a species enhanced by a factor of 4 or 5 (for example) then the ultimate bulk detection limit is on the order of 200–300 ppm. While the surface detection limit for ESCA is moderate, the ultimate bulk detection limit may be good because of surface segregation.

CONCLUSIONS

This work presents quantitative surface analysis by ESCA of Mt. St. Helens Ash, and NBS Standards 1648 and 1633a. A general quantitative method has been used to establish surface composition data for these samples, useful for future referencing. Surface detection limits for ESCA are on the order of 0.1% by weight. However, for species segregated at the surface, and thus enriched in concentration, the minimum detectable concentration in the bulk can be ca. 200–300 ppm. These analyses have also allowed identification of surface species, without destructive depth profiling.

Credit

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