A METHOD FOR TOTAL ANALYSIS OF MINOR AND TRACE ELEMENTS IN THE SOIL CLAY FRACTION TO ATMOSPHERIC AEROSOLS.

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ABSTRACT

Several methods recommended for soil analysis using acid digestion were tested for the total analysis of minor and trace elements of the clay fraction. The proposed method using mixtures of $HClO_4/HF$ was adequate to dissolve the clay. The recovery results ranged from 84-116% for Cr and Zn respectively. The clay fraction from four sites located in an area surrounding a copper minefield (VI Región, Chile) was analyzed for the elements Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, using atomic absorption spectrometry. Na and K were determined by flame photometry. The origin of the trace elements occurring in the atmospheric aerosols, is redetermined using the results obtained by the modified method of analysis proposed in this paper. The use of the enrichment factors (EF) calculated from the composition of the local clay and the coefficients of variation are proposed as a better criterion than the EF calculated from the composition of terrestrial crust. An actual atmospheric contamination with Cu, Zn and Pb was found in the studied area.
Additional index words: Soil clay dissolution, new enrichment factors, atmospheric pollution.

INTRODUCTION

One of the sources contributing to the airborne particulate matter is related to the soil particles blown by the wind (1). These particles, that remain suspended in the air due to their small diameter, correspond mainly to the clay fraction.

The atmospheric aerosols contain trace elements whose origin can be established by the criterion of the enrichment factor (EF), at least as a first approximation (2).

This criterion introduces the mean elements concentration of the terrestrial crust. The EF is usually calculated using Mason's international mean values of samples taken within a depth of several kilometers (3).

The presence of soil particles in the atmosphere is closely related to the local composition of the soil being subjected to the eolic erosion process. In fact, the lighter the soil particles, the more likely they are to remain suspen

ded in the air; therefore, in order to obtain a more precise ascription for the origin of the elements in a given site, the minor and trace element contents of the clay fraction should be known.

The purpose of this work was to study a chemical procedure to determine by atomic absorption spectrophotometry, most of the minor and trace elements in the soil clay fractions that can occur in the atmospheric aerosols. These values were used to determine the origin of the trace elements.

MATERIALS AND METHODS

Four soil samples were taken from an area surrounding a copper minefield at a depth of 0-5 cm. The samples were dried and screened through a 2-mm sieve.

The clay fractions of 20-g soil samples were separated by ultrasonic treatment after the removal of the organic matter by H_2O_2 (4). The sonic treatment was repeated until the supernatant solution became clear. The clay suspensions were flocculated by adding 0.05 N HNO_3 to avoid the adsorption of basic cations (Ca^{++}, Mg^{++}, K$^+$ and Na$^+$) and were washed five times by centrifugation with the same reagent to remove all the exchangeable cations. Finally, the clays were washed twice with 70% ethanol (4), dried at 105 °C to determine the clay content, and screened through a 0.1-mm sieve.

Some of the chemical characteristics of the soils sampled are given in Table I. The organic matter was analyzed by the Walkley-Black method (5) and the soil particle size distribution by the Bouyoucos method (6).

TABLE I. Chemical characteristics of the soils sampled.

Sampling Site	Soil classification [+].	pH[++]	Organic matter	Sand	Silt	Clay
					%	
Coya	Inceptisol	5.1	3.65	28.9	43.9	32.0
Sauzal	Entisol	6.9	0.43	40.9	22.0	42.7
La Compañía	Inceptisol	6.7	1.97	36.8	21.6	46.2
Codegua	Inceptisol	6.5	7.41	5.0	30.2	68.3

+   DIPROREN - SAG, Ministry of Agriculture, Chile.
++   Measured in the soil/water relation of 1/2.5.

The total analysis was carried out after dissolving the clay fraction by the wet digestion procedure proposed in this work and described in the following section. This procedure was achieved after testing the methods of Jackson (4) and Chowdhury & Das (7) with some modifications according to the method given in the following section of this work.

The elements Mg, Ca, Cr, Mn, Fe, Co, Ni, Zn, Cd and Pb were quantified by atomic absorption using a Perkin Elmer Model 360, Atomic Absorption Spectrometer. Ca and Mg were determined in the presence of 2000 ppm of Sr as internal standard. Na and K were determined by flame photometry using an Evans Electroselenium equipment.

The results are reported on the basis of clay dried at 105 °C. Sample results are the average of at least four determinations, except in the first two procedures tested for the dissolution of the clay fraction, where duplicate determinations were performed.

Recovery studies of the dissolution method proposed, are based on multi-ele ment standard solutions prepared to contain known concentrations of the ele -- ments of interest. Aliquots of these solutions were subjected to the same trea tment as the clay samples.

RESULTS AND DISCUSSION

Initially, the method recommended by Jackson (4) was used, however,   even after repeating the treatment a white residue remained.

Since the presence of any precipitate in the extracts can cause erroneous results, the procedure given by Chowdhury and Das (7) was tested. One   method differs from the other in the ratio of HF/HClO$_4$; Jackson uses a 10:1   ratio while Chowdhury and Das 4:1.

As the precipitate persisted with the Chowdhury and Das method, several mo difications were done using the soil sampled in Coya.

The results obtained for all the elements analyzed showed that only the con tent of Mg and Co are dependent on the method of dissolution employed.   For this reason, the data in Table II refer to these two elements only.

TABLE II.   Mean concentrations $(\bar{x})^+$ and standard deviations (s.d.) of Mg and Co obtained for four modifications of the clay dissolution method in Coya soil.

Modifications	Mg (ppm)	Co (ppm)	
I	7248 ± 0	58 ± 0	I : Modification to Jack- son method.
II A	8367 ± 476	47 ± 5	II: Modifications to Chow dhury and Das method.
II B	9310 ± 134	61 ± 0	
II C	8904 ± 62	70 ± 6	

+ : Number of determinations greater than two.
I : Jackson method applied twice.
II A : Control of temperature and time digestion; addition of H$_3$BO$_3$ at final step.
II B : Addition of H$_3$BO$_3$ after heating with HF, but not at final step.
II C : Treatment with mixture HF/HClO$_4$ applied twice   and elimination of treatment with HClO$_4$.

The method of dissolution finally used and recommended in this paper was   as follows: 0.5-g sample (air-dried), accurately weighed, was placed in an approxi mately 30-ml platinum crucible and moistened with a few drops of water;   10 ml of HF and 2.5 ml of HClO$_4$ were added and the crucible was almost completely co vered. The mass was kept one hour at controlled temperature (180-220 °C)   on a hot plate for complete dissolution and then evaporated to dryness. After cool - ing, 5 ml of HF and 0.5 ml of HClO$_4$ were added and the crucible was heated (al ways at 180-220 °C) to evaporate the mixture until HClO$_4$ fumes were observed. After cooling, 10 ml of 4% H$_3$BO$_3$ and 5 ml of 1:1 HClO$_4$ were added and the mixtu re was heated to boiling. Before cooling, the solution was transferred to a 50

ml volumetric flask, cooled and diluted to the mark (if under these conditions
a white precipitate still remains, the solution in the volumetric flask can be
warmed in a double boiler). A blank was prepared in the same way. The   whole
procedure took about 3 hours.

The mean concentrations of Mg and Co, with coefficients of variation   less
than 10% for the method proposed in this paper, always turned out to be higher
than the concentrations obtained using the Jackson method. This fact confirms
the initial assumption that the presence of any precipitate in the final solu-
tion can occlude part of the elements analyzed. The X-ray analysis of the per-
sistent white precipitate (modification II B) indicated the presence of fluori_
de with high content of Mg.

The recovery results obtained for each element are shown in Table III. The-
se values were used to correct the concentrations of the elements determined
in the clay fraction of the four soils studied. These concentrations are given
in Table IV.

TABLE III. Mean recovery values of minor and trace elements in the clay
            samples.

	Elements												
	Na	Mg	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Recovery %	102	109	102	94	84	89	104	102	106	106	116	95	92
Standard deviation	0,0	8,2	19,2	0,7	0,0	3,5	3,9	10,3	15,5	1,4	5,0	2,5	0,0
Concentration level (ppm)	5	1-2	5-10	10	1,4	1,4	10	0,07-2	0,6	1,8	0,28	0,07	2,8

TABLE IV. Mean concentrations ($\bar{x}$) and standard deviation (s.d.) for the
          elements of the clay fraction.

	Elements												
	Na	Mg	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
	Coya												
$\bar{x}$ (ppm)	4508	8904	10824	2258	40.4	1294	72977	70	47.6	168	166	5.2	95.3
s.d.	2840	62	1716	373	6.0	117	3484	6	9.5	12	12	2.1	12
n^+	11	3	11	11	13	13	13	2	11	12	12	12	12
	Sauzal												
$\bar{x}$ (ppm)	7360	17820	10755	5004	23.1	3006	78541	103	43.0	276	159	5.2	111
s.d.	3856	1223	1294	1080	0.2	683	3890	0	6.5	40	19	2.1	6.4
n	7	3	6	7	5	7	7	2	6	7	7	4	5
	La Compañía												
$\bar{x}$ (ppm)	10299	17377	16026	5850	35.6	1232	87242	93	42.9	655	239	6.3	201
s.d.	5234	581	2821	1706	6.4	148	6180	25	2.6	31	31	1.0	8.0
n	6	2	5	6	5	6	6	2	5	5	6	6	6
	Codegua												
$\bar{x}$ (ppm)	7480	18318	18801	5017	42.8	1114	75361	72	45.8	214	148	6.3	99.2
s.d.	751	590	2042	542	6.2	96	4877	4	3.9	38	17	2.1	7.0
n	6	4	6	6	7	7	7	2	6	6	6	7	7

n^+ : Number of determinations.

The highest content of Na, Fe, Cu, Zn and Pb was found to occur in the La Compañía soil, whereas the highest content of K corresponded to the Codegua soil; the highest content of Mn and Co was observed in the Sauzal soil. It should be noted that the highest value observed for Cu (La Compañía) and Mn (Sauzal) was about three times higher as compared to the other soils. The con tents of Ni and Cd were similar in all the soils studied. On the other hand, the contents of Ca and Mg were low in the Coya soil.

Table V shows a comparison of the concentration range of minor and trace e lements obtained in soil clay fraction by Bear (9), in the terrestrial crust by Mason (3) and in this work. Comparison of the results of this report with the values obtained by Bear shows relative coincidence only for Mg, K and Fe, while the contents of Na and Mn are higher and the content of Ca is lower. Comparing the results of this report with those of Mason for the terrestrial crust it is observed that:

TABLE V.   Concentration range of minor and trace elements in clay and terres-
            trial crust.

| Element | Clay | | Terrestrial crust |
	This work	Bear (9)	Mason (3)
		ppm	
Na	1600 - 15500	440 - 1780	24000
Mg	8900 - 19000	12600 -16200	19500
K	9400 - 20900	12000 -36300	21000
Ca	1800 - 7500	6860 -36000	42000
Cr	23 - 49	-----	100
Mn	1000 - 3700	570 - 630	950
Fe	69500 - 93500	68300 -80400	56000
Co	68 - 103	-----	25
Ni	40 - 57	-----	75
Cu	155 - 690	-----	55
Zn	140 - 270	-----	70
Cd	3 - 8	-----	0.2 (11)
Pb	84 - 210	-----	12.5

-       For Mg, K, Mn and Fe concentrations practically agree with those of Mason
        (3).

-       The concentration values of Cr, Na, and Ca are lower by a factor of four
        for Cr up to a factor of twenty-three for Ca.

-       The concentration values of Zn, Co, Cu, Pb, and Cd are higher by a factor
        of two for Zn up to a factor of forty for Cd.

These results show that for some elements there are significant differences between their local concentrations in the clay and the corresponding mean con centrations for the terrestrial crust. In these cases, it may be possible   to assume that the conclusions relative to the origin of the elements obtained from the enrichment factors could be modified, if their absolute values change significantly.

In atmospheric pollution problems the concept of enrichment factor (EF)   is widely used because it is directly related to the origin of the elements   in the atmosphere.

The EF calculations are generally based on concentrations of elements   in

TABLE VI. Range and mean concentration ($\bar{C}$ *) from some trace elements in atmospheric aerosols sampled in the studied area including their variability (V) and their coefficients of variation (CV).

		Fe	Mg	Cr	Mn	Ni	Cu	Zn	Pb
Coya (n ** = 10)									
Range		634-23729	219-2914	0.0-5.6	26.3-596	0.0-2.6	38.4-537	0.0-889	0.0-4660
$\bar{C}$ (ng/m³)		11606	1489	0.9	292	1.0	260	141	680
V		8597	957	1.9	213	1.0	170	263	1416
CV (%)		74	64	211	73	104	65	186	208
Sauzal (n = 9)									
Range		316-4431	71-791	0.0-2.8	6.5-104	0.0-105	48.3-160	0.0-86.8	4.4-32.2
$\bar{C}$		2547	467	0.3	62.6	12.6	92.8	23.3	13.7
V		1065	166	0.9	26.3	33.5	32.7	27.4	7.3
CV (%)		42	36	290	42	266	35	118	53
La Compañía (n = 10)									
Range		1014-18292	133-3617	0.0-93.6	20.5-303	0.0-150	61.2-512	0.0-438	26.1-137
$\bar{C}$		9286	1840	13.1	173	27.4	176	124	59.3
V		4972	1028	27.9	91.6	43.5	121	152	29.1
CV. (%)		54	56	213	53	159	69	123	49
Codegua (n = 10)									
Range		1752-20529	157-3345	0.0-18.5	25.4-289	0.0-47.4	63.5-183	0.0-157	23.1-104
$\bar{C}$		9841	2103	8.7	186	11.8	97.5	54.0	42.2
V		5336	1050	7.9	94.7	13.9	33.5	50.4	23.7
CV (%)		54	50	91	51	118	34	93	56

* : from Ref. 10

** : number of atmospheric aerosol samples.

TABLE VII. Mean enrichment factors (EF) for some elements in atmospheric aerosols calculated from the composition of the clay and the terrestrial crust including their variability (V) and their coefficients of variation (CV).

In each data cell the two numbers correspond to the values calculated from the clay and from the terrestrial crust respectively (Ni has a single value).

Elements

		Mg	Cr	Mn	Ni	Cu	Zn	Pb
Coya (n* = 10)	EF	1.5** / 0.4#	0.6 / 1.2	1.5 / 1.4	1.1	16.6 / 34.3	5.0 / 8.2	11.2 / 56.4
	V	0.7 / 0.2	1.3 / 2.3	0.3 / 0.3	1.9	14.2 / 29.8	6.4 / 10.4	18.7 / 94.0
	CV (%)	47 / 50	217 / 192	20 / 21	173	86 / 87	128 / 127	167 / 167
Sauzal (n = 9)	EF	0.9 / 0.5	0.1 / 0.5	0.6 / 1.3	2.5	15.4 / 49.2	11.6 / 16.8	4.4 / 23.8
	V	0.1 / 0.1	0.2 / 1.4	0.1 / 0.2	2.9	13.3 / 42.3	17.2 / 25.0	2.3 / 12.4
	CV (%)	11 / 20	200 / 280	17 / 15	116	86 / 86	148 / 149	52 / 52
La Compañía (n = 10)	EF	1.0 / 0.5	1.4 / 6.8	1.3 / 1.0	5.7	3.5 / 23.9	6.8 / 13.1	4.9 / 43.0
	V	0.2 / 0.1	2.3 / 11.2	0.2 / 0.2	8.9	2.5 / 17.6	6.9 / 13.5	5.9 / 52.0
	CV (%)	20 / 20	164 / 165	15 / 20	156	71 / 74	99 / 103	120 / 121
Codegua (n = 10)	EF	0.9 / 0.5	1.3 / 4.4	1.3 / 1.0	4.1	5.7 / 14.7	8.1 / 11.4	6.2 / 31.7
	V	0.2 / 0.1	1.7 / 5.9	0.3 / 0.2	4.8	4.2 / 10.7	12.3 / 17.3	7.1 / 36.2
	CV (%)	22 / 20	131 / 134	23 / 20	117	74 / 73	152 / 152	115 / 114

* Number of atmospheric aerosol samples.

** Data calculated from the composition of the clay.

\# Data calculated from the terrestrial crust.

the terrestrial crust. The calculation includes, for each element, the ratio between the relative concentrations found in the local air and in the average soil. The relative concentrations are referred to a given element, Fe in this case, whose occurrence in the air is only from a natural origin.

Data about the composition of some trace elements in atmospheric aerosols sampled in the area studied in this research are given in Table VI. Using this information, the EF values were calculated from the composition of the local clay and of the terrestrial crust; the results are given in Table VII.

Considering the EF values near the unit and the low coefficient of varia - tion (CV) found for Mg and Mn, a clear natural origin can be ascribed to both elements. The origins for Cr and Ni seem to be more complex; even though the EF values are low, they must have an anthropogenic origin because of the high CV observed for their EF.

The EF calculated for Cu, Zn, and Pb according to Mason are much higher than the unit, showing an anthropogenic origin. In some cases the EF calcula- ted from the composition of the local clay hinder the clear and direct ascrip tion of the origin, but when the CV are analyzed, the high values observed are an indication that the origin must certainly be anthropogenic. The diffe- rences observed in EF are due to the occurrence of clays rich in Cu as compar ed with the values given for the terrestrial crust.

CONCLUSIONS

The methods of dissolution recommended by Jackson and Chowdhury and Das are not adequate for the total dissolution of the soil clay fraction. Modifi- cations including one hour digestion time with $HF/HClO_4$, a second treatment with this acid mixture and the addition of H_3BO_3 in the final step of the ana lysis, are required.

For some elements there are significant differences between their local concentrations determined in the clay and the corresponding mean concentra -- tion values reported for the terrestrial crust.

The EF calculated from the composition of the local clay would be a better indicator to detect pollution problems. On the other hand, CV should be al- so considered in the origin attributed to the elements occurring in the atmos pheric aerosols.

ACKNOWLEDGMENTS

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