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Work in the coordinated programme on neutron activation analysis of pollutants in human hair, using research reactors

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FINAL REPORT

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Institute where research is being carried out:
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Neutron Activation Analysis Of Pollutants In Human Hair Using Research Reactors

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Jan. 1978 - Dec. 1978

INTRODUCTION

During the last few years human scalp hair, a horny fibrous derivative of the skin, became well recognized as an invaluable tissue for monitoring human environmental exposure (1 - 11). The sequential accumulation of a number of elements in particular (growth rate of hair strands ca o,3 mm / day), the fact that the concentrations of trace elements in hair [illegible] at least an order of magnitude greater than in the body fluids and other accessible tissues, as well as the simple obtainment and the easy preparation of the specimen, reveal the advantages of this test material.
Therefore systematic analyses of concentrations and distribution of 6 elements (As, Sb, Cd, Hg, Br and Zn) in hair samples obtained from population groups of four Austrian provinces (Bundesländer) were accomplished by INAA (instrumental neutron activation analysis).

1. Wien (2oo samples = o,o15% population) +
2. Burgenland (loo samples = o,o4o% population) +
3. Vorarlberg (loo samples = o,o33% population)
4. Ost- Tirol (44 samples = 0,1oo% population)

(+ analyses were carried out 1977)

The selection of those regions are based on the distinct economic structure caused by the geographical location as well as the heterogenous geological structure of the country, which is to be illustrated in table I and an index map.

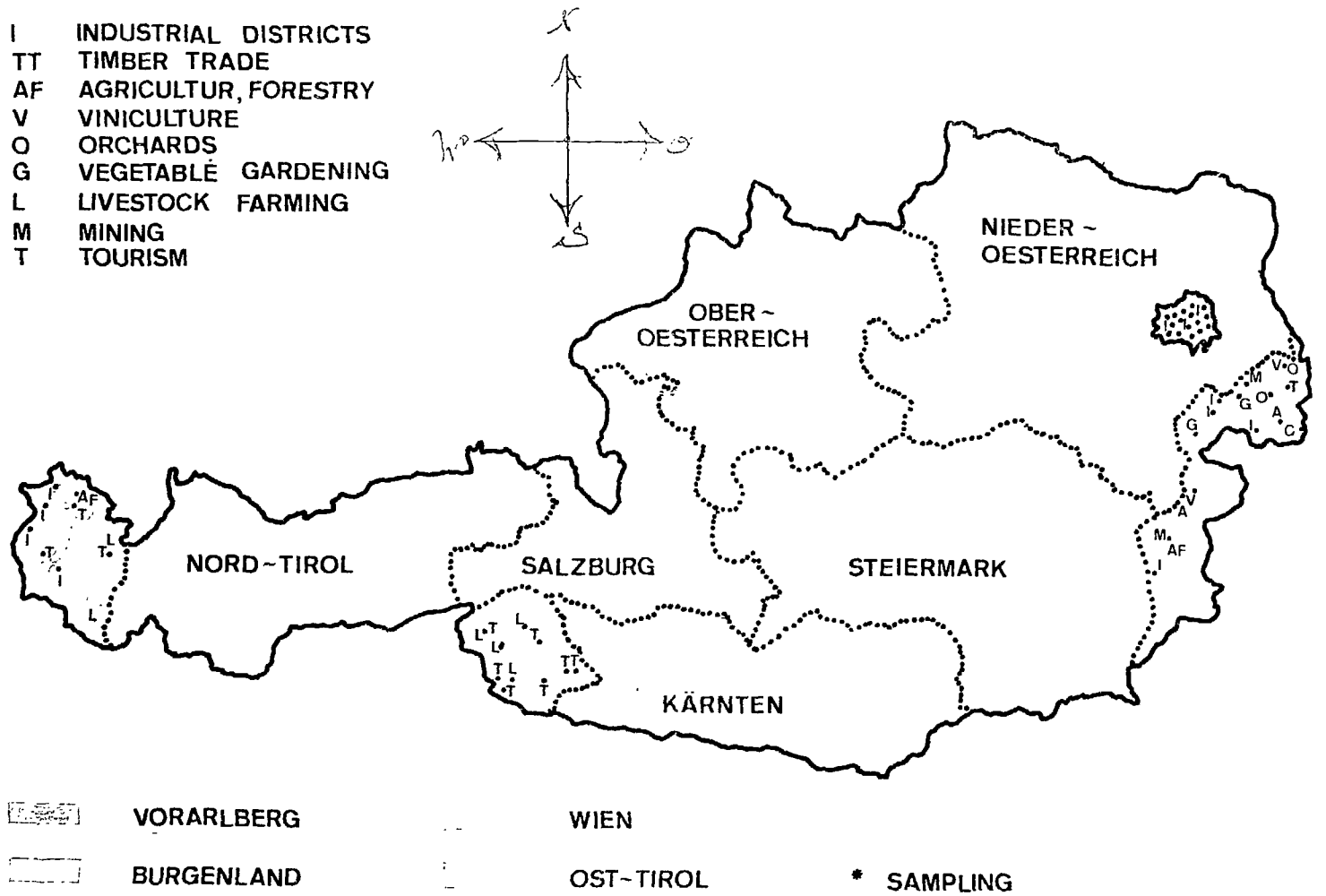
I INDUSTRIAL DISTRICTS
TT TIMBER TRADE
AF AGRICULTUR, FORESTRY
V VINICULTURE
O ORCHARDS
G VEGETABLE GARDENING
L LIVESTOCK FARMING
M MINING
T TOURISM
NIEDER ~ OESTERREICH
OBER ~ OESTERREICH
NORD ~ TIROL
SALZBURG
STEIERMARK
KÄRNTEN
VORARLBERG
BURGENLAND
WIEN
OST ~ TIROL
* SAMPLING

Table I

region	agriculture forestry	industry	commerce	others
Wien	1 %	39 %	2o %	4o %
Burgenland	4o %	4o %	8 %	12 %
Vorarlberg	6 %	58 %	14 %	22 %
Ost- Tirol	timber cattle	5 %	timber cattle	tourism

EXPERIMENTAL

Hair Sampling

The hair strands were clipped close to the scalp from 6-8 spots distributed over the head. 1o cm sections of the strands were used for routine analyses, cutting off the distal ends. Stainless steel scissors were used for clipping because Fe nor Cr were to be determined. The total weight of the samples amounted to 8o - 1oo mg.

Hair Treatment

In order to remove oily material from the specimen and with adhering dust as well as a large fraction of NaCl, the hair strands were washed in quartz beakers with five 1o -minute contacts (manual shaking) with 25 ml portions of successively aceton, water, water, water, aceton.
Before using the liquids the purity was checked by NAA.
After washing the samples were air dried at room temperature and 5o - 7o mg of the specimen were weighed into the irradiation containers and sealed tightly.

Quartz

Since longlived isotopes only were to be determined quartz was used for container material.
The vials were made in the laboratory. The smallest HERALUX-tubes (Heraeus), one meter in length, 3,5 mm inner diameter, o,5 mm wall thickness, were cut into 4o mm pieces. The weight of the ampoules varied between 5oo - 6oo mg, which still was com-

parable with the weight of the samples.
Through the low weight of the ampoules the additional activity of the quartz, a displeasing accompanying phenomenon in INAA, could be reduced to a minimum.
Various HERALUX tubes showed a number of metal impurities in variable concentrations but the particular tubes (24 ampoules) showed an excellent homogeneity over the whole length, that it proved to be sufficient to activate a blank simultanously with the samples. The blank represented the quartz background and was used for subtraction.
The sealing of the ampoules was done by means of an carbon arc.

Reference Sources

In my opinion slightly acidic solutions of inorganic compounds or pure metals are the most exact reference sources because one can select the particular elements and the appropriate concentrations. By this means, an additional activity, which in any case appears using " mixed " reference sources is eliminated.
For the stock solutions of As, Cd, Sb, Hg and Zn Merck Titrisoles were used.The Bromine standard was prepared from KBr.
The water, needed for all dilution processes, derived from a MILLIPORE filter system with 3 columnes: graphite, " mixed bed " ion exchanger, millipore filter o,8µ pore size. It is a by pass-system and bi- or tridistilled water is used as starting solution. The extrem purity of the final product is realized by the re - sistance of 18 MΩ. cm .
Preparing the standards, 1 µl of the standard solutions were spotted on filter strips (Blauband- Filter, Schleicher-Schüll, 2 x 15 mm) and two strips together (As-Hg, Br-Zn, Cd-Sb) were placed into the ampoules, which were sealed immediately.
As regards impurity concentrations expected in the hair samples the concentrations of the standard solutions of the particular elements were prepared with the same order of magnitude.

Activation

The activation processes were carried out in the ASTRA-Reactor Seibersdorf, Austria.
For all experiments the activation period took 18 hours at a

neutron flux of $7.1o^{13}$ $n.cm^2/$ sec in a corner position of the reactor core. The uniform activation of ONE SAMPLE UNIT (12 hair samples, 3 vials with the standards and 1-2 blanks) was guaranteed by means of a rotation facility.

Measurements

After a cooling period of 72 -96 hours the analysis for the radionuclides of As, Sb, Cd and Br was accomplished by instrumental gamma- spectroscopy. The concentrations of Hg and Zn have been measured three weeks later.
A well shielded Ge-Li detector (48cc, 3 KeV Co, 3% eff. 1:2o), coupled to a multi-channel pulse-height analyzer with 2o48 channels was used.
To avoid the high background in the low energy region caused by the betas of the sulphur, a lucite absorber of 2o mm thickness was placed between sample and detector.
Dead time correction was unnecessary because the counting rates seldom exceeded looo cts / sec, in spite of the fact that the samples were measured " CONTACT ".
Nevertheless a few number of samples showed counting rates between 5.ooo- 5o.ooo cts / sec caused by an extremly high Bromine-activity. These samples had to be eliminated because the triplett Br-As-Sb (o,554 -o,559- o,564 MeV) could not be resolved instrumentally.
The evaluation of the spectra was accomplished by means of a PDP 11/1o computer.

RESULTS

As it is pointed out in the introduction hair samples of the population of four different regions in Austria were analyzed for As, Sb, Cd (toxic elements), Zn (essential) Sb and Br (little is known about their function in the body) expecting that the elemental distribution as well as the concentrations of the quoted elements would characterize the very distinct life-long habits as well as the different working conditions.

Taking into consideration the economic situation in Ost - Tirol, a region with mainly rural population subsisting chiefly on cattle farming, timber working and tourism, without considerable industry and in many respects somehow behind the times, one is led into temptation to assume this part of Tirol could present a region, where pollution of air, soil and water might still be neglected.
Thus, one would detect " NORMAL " concentrations and distributions of the six elements in hair samples obtained in Ost-Tirol. Therefore hair samples collected in industral districts and towns must show increased concentrations of As, Sb, Cd, Hg and Br, and even hair samples obtained in aereas where agriculture is prevailing higher Hg-contents could be expected on account of using mercury compounds for seed dressing.
The results are compiled in table II and will be explained as follows:
Elements known to be essential in the body show normal distribution (12).
For the majority of trace elements the standard deviations are equal or higher than the arithmetic means. Therefore in the case of trace elements the characteristic distributions are close to log normal. Thus the geometric means (G.M.) multiplied or divided by the antilog of σ (standard deviation) give a better characterisation of the distributions than the arithmetic means with the corresponding deviations.
Aside from this another fact is expressed by antilog σ: essential elements, such as zinc, show a tendency to low antilog σ in cases where these elements enter the body in concentrations which are necessary for the normal physiological processes.
Trace elements, on the contrary, tend to higher antilog σ and the numerical values indicate whether the concentrations can be denoted quite normal or " contamination" must be considered, as it is demonstrated by the histogram (fig 1) of As and Sb in the Burgenland samples.
If the particular regions are compared with each other it is to be recognized that indeed the hair samples of Ost-Tirol, on the average, show the lowest contents in environmental metals.

The second place is taken by Vorarlberg, a region which is highly industrialized only in the West (textiles), followed by Wien with the characteristica of a large town.
The order of succession was, by no means, amazing but the concentration levels themselves compared with the results published by other authors (13, 14) were quite surprising because the concentrations are moving between considerable low limits.
The results obtained from the Burgenland samples, on the other hand, show just the opposite. The high concentration levels and the abnormal shape of the distribution curves of As and Sb but also the increased Cd and Zn contents show very clearly the influence of the mining districts.

CONCLUSION

These studies have demonstrated that analysis of scalp hair for toxic metals provides a valuable means of assessing relative exposure of population groups and has advantages over blood or urine testing. The analysis of hair is accomplished readily and with good accuracy by nuclear activation mehtods partly because the concentrations are at least an order of magnitude greater than in body fluids or other accessible tissues.

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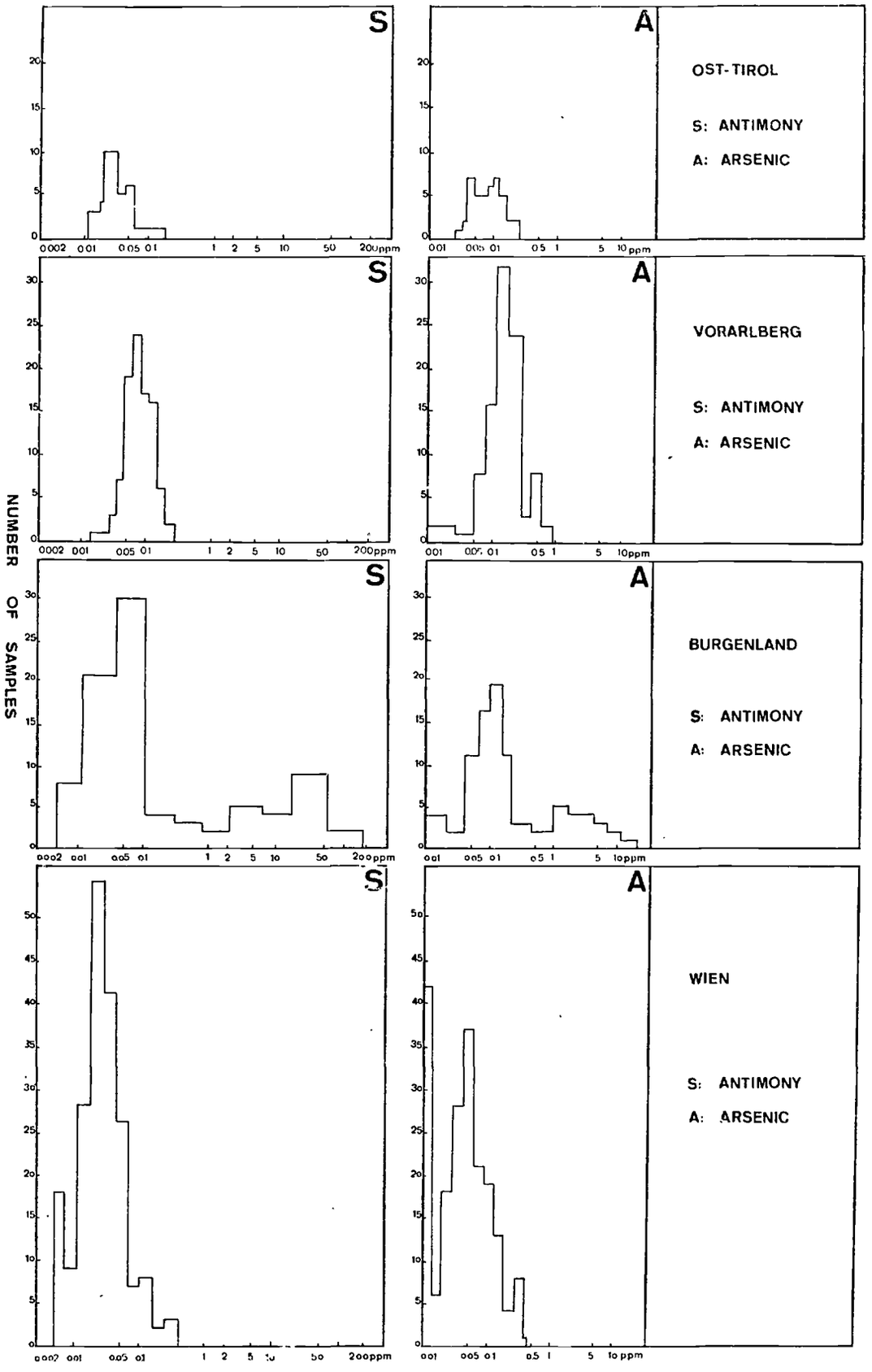
Table II

element	Bundesland	Geom. Mean	x̊	Antilog σ	Median	PPM - Range	numb.sam.
As	Ost - Tirol	o,o773	x̊	1,6895	o,o79	o,o25- o,254	39
	Wien	o,o434	x̊	2,7o52	o,o47	o,olo- o,399	197
	Burgenland	o,1536	x̊	6,o734	o,o85	o,olo- 19,43o	89
	Vorarlberg	o,1o62	x̊	1,9826	o,1o8	o,olo- o,619	96
Sb	Ost-Tirol	o,o363	x̊	2,2295	o,o35	o,o13- o,228	41
	Wien	o,o279	x̊	2,3433	o,o27	o,oo5- o,423	196
	Burgenland	o,1845	x̊	15,781o	o,o57	o,oo5- 186,89o	89
	Vorarlberg	o,o351	x̊	1,6893	o,o35	o,oo6- o,131	96
Cd	Ost-Tirol	o,7658	x̊	1,5145	o,79	o,26 - 1,97	41
	Wien	o,7283	x̊	2,166o	o,79	o,o8 - 4,4o	198
	Burgenland	o,8261	x̊	2,644o	o,99	o,o8 - 3,18	94
	Vorarlberg	o,8461	x̊	1,8492	o,86	o,2o - 6,12	96

element	Bundesland	Geom. Mean	$\dot{x}$	Antilog σ	Median	PPM - Range	no.of samp.
Hg	Ost - Tirol	o,5254	$\dot{x}$	2,2881	o,5o	o,14 - 36,54	44
	Wien	o,642o	$\dot{x}$	1,7136	o,66	o,1o - 2,3o	2oo
	Burgenland	o,4648	$\dot{x}$	1,5747	o,45	o,13 - 1,36	94
	Vorarlberg	o,5668	$\dot{x}$	1,7382	o,57	o,o5 - 1,95	1o2
Br	Ost - Tirol	2,55	$\dot{x}$	3,11	2,78	o,15 - 36,52	4o
	Wien	2,o5	$\dot{x}$	3,57	1,99	o,o8 - 86,84	197
	Burgenland	2,92	$\dot{x}$	3,26	2,82	o,27 - 56,25	88
	Vorarlberg	4,55	$\dot{x}$	3,o7	3,86	o,46 - 49,7o	96
Zn	Ost - Tirol	155	$\dot{x}$	1,2	152	8o - 265	44
	Wien	14o	$\dot{x}$	1,3	14[illegible]	47 - 273	2o1
	Burgenland	151	$\dot{x}$	1,7	153	5o - 486	94
	Vorarlberg	177	$\dot{x}$	1,3	181	76 - 333	1o2


S
A
OST-TIROL
S: ANTIMONY
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VORARLBERG
BURGENLAND
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NUMBER OF SAMPLES
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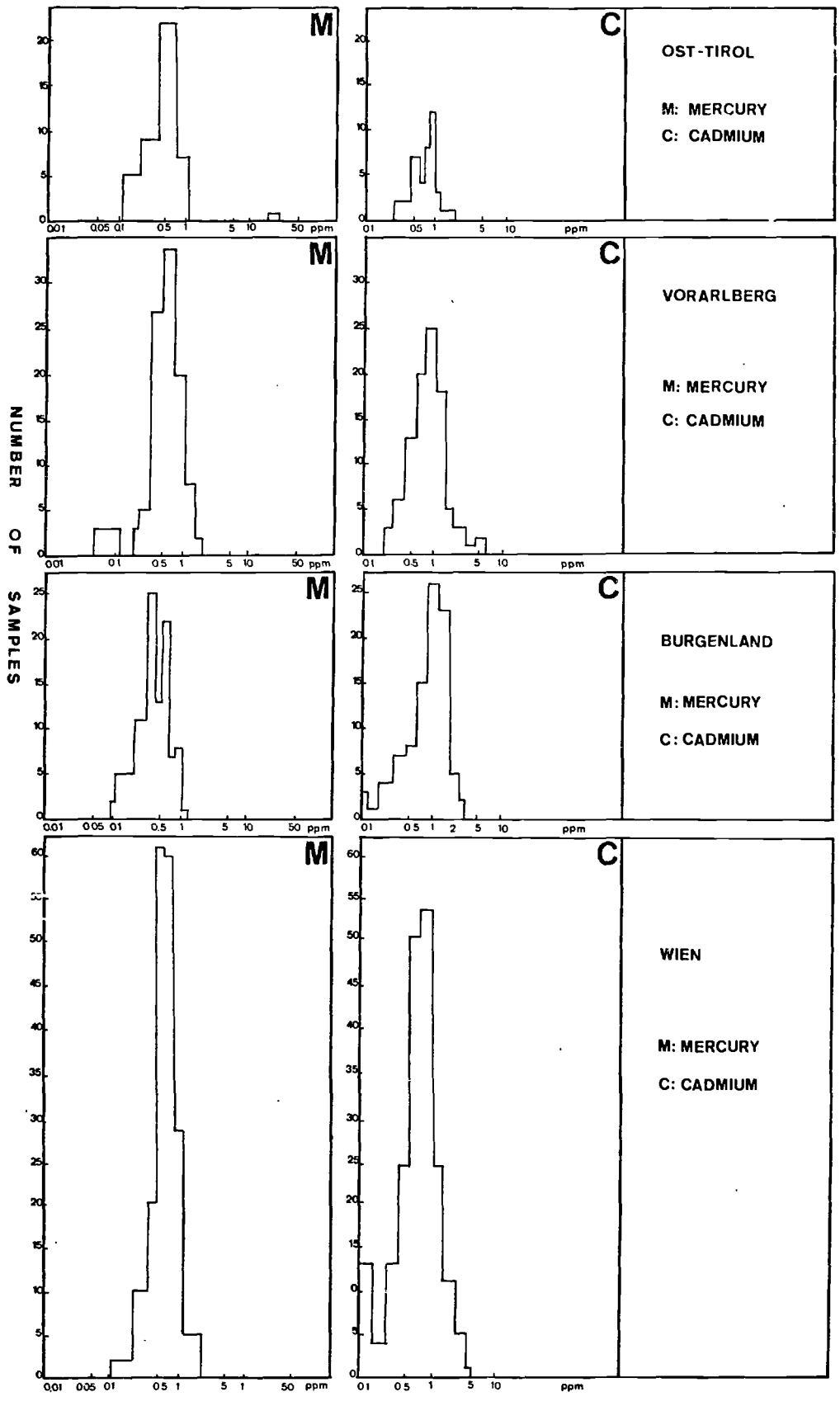
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WIEN
M: MERCURY
C: CADMIUM
NUMBER OF SAMPLES
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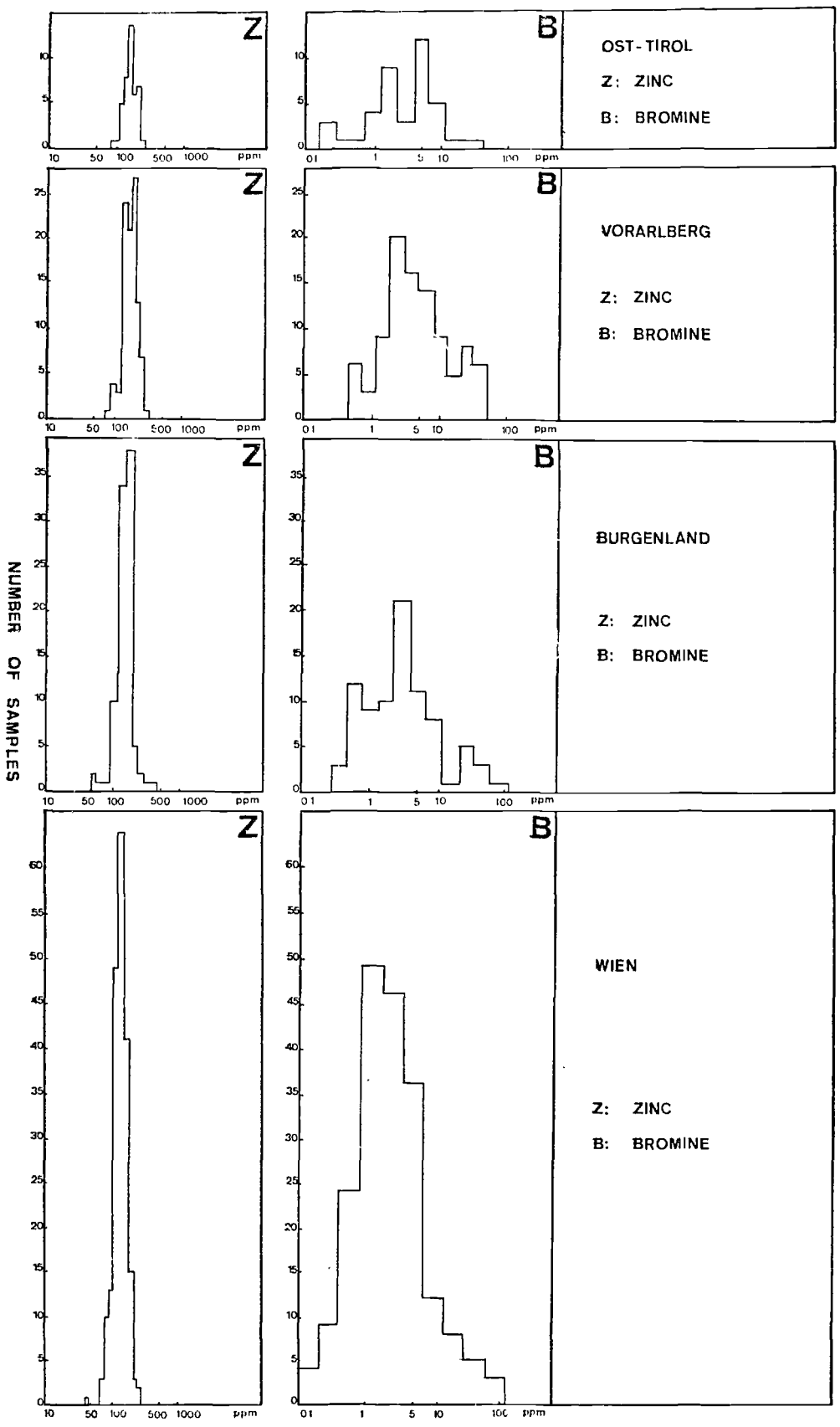
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OST-TIROL
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NUMBER OF SAMPLES
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