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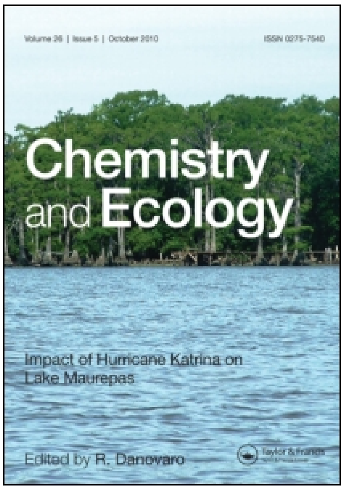

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Analysis of Trace Elements in Natural Waters†

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The results of the research project on the hydrogeochemistry of natural waters of the Latium Region clearly show that natural processes are responsible for a very high variability of some trace elements. This is important in order not to attribute to pollution relatively high levels depending on natural processes, such as the leaching of peculiar geological formation and/or hydrothermal circulation.

Trace element analysis in natural waters is one of the hardest fields of analytical chemistry. This is mainly due to the difficulties arising from storing, handling and transporting the sample by adding or subtracting a number of the elements to be determined.

The analytical instruments provided by the present technology are not capable, moreover, of detecting the very low levels generally found in unpolluted natural waters. In order to overcome these difficulties, complete analytical procedures have been devised, tested and widely applied to hydrogeochemical studies at the ENEA's Environmental Geochemistry Laboratory.

Briefly, the analytical procedures set up for many elements are based on the solvent extraction of metal chelates in the field, immediately after the sample has been collected and filtered at 0.45 μm. The extracts are stored in Pyrex test-tubes and brought to the laboratory, where acid back extraction is used before trace element analysis is carried out by Flameless AAS Analysis.

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In order to lower the blank values, and therefore to enhance the actual sensitivity, it has been necessary to purify many reagents as well as glassware and polyethylene bottles.

In the last years detection limit is the most frequently, and almost only, term used in AAS analysis in order to get an overall idea of the sensitivity. This term is not well suited when comprehensive analytical procedures are used because its meaning is strictly related to the instrumental analysis. When using analytical procedures and their related variability, blank values are the most important reference point for the overall reliability of the analytical data. Therefore, a complex effort has been made in order to estimate the blank values and the relative standard deviation; Table I shows the results of blank values and the lowest detectable concentration, obtained in numerous tests.

As regards accuracy and precision values, our procedures are characterized by values of 15% and 5% respectively referring to tests between batches.

TABLE I
Blank values and lowest detectable concentration for some elements of the adopted analytical procedures referring to routine conditions, i.e. starting from a 200 ml water sample aliquot

	Blank value	Lowest detectable concentration ng/l
Pb	10	15
Cu	15	20
Cd	2	3
Se	2	3
As	3	5
Hg	1	2

OPERATING PROCEDURES

The outline of the complete analytical procedures is shown in the scheme of Figure 1 and Table II.

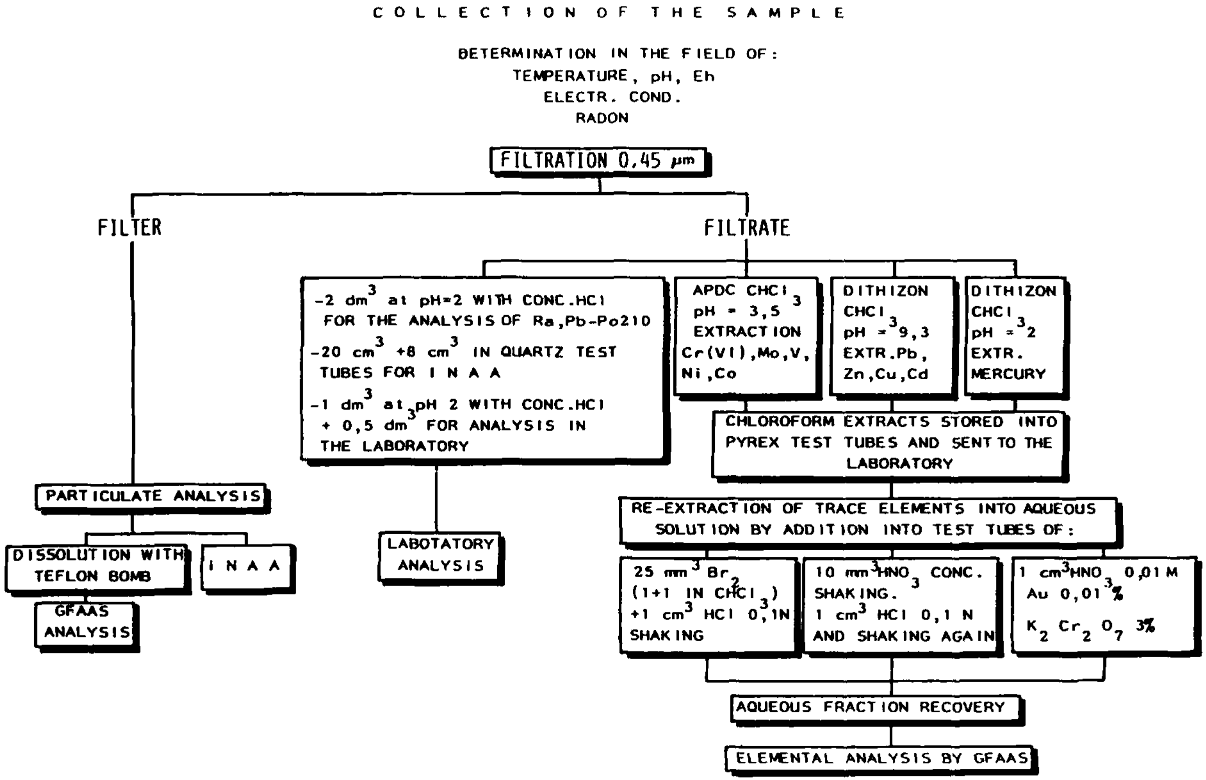

FIGURE 1 Scheme of the analytical procedures.

TABLE II
Laboratory analyses

Ca, Mg	EDTA titration or flame atomic absorption
Na, K	Flame emission or flame atomic absorption
Li, Rb, Cs	Flame emission scanning (Dall'Aglio e Visibelli 1974)
Sr	Flame atomic absorption
SO_4	Turbidimetry or Autoanalyzer or Ionic Chromatography
Cl	Autoanalyzer or Ionic chromatography
SiO_2	Spectrophotometry molybdenum blue solution or Autoanalyzer
B	Spectrophotometry 1–1' dianthrimide solution or Autoanalyzer or ICP
F	Specific electrode or Spectrophotometry Alizar complex solution or Ionic Chromatography
NH_3	Specific electrode or Autoanalyzer
No_3–NO_2	Autoanalyzer
P	Autoanalyzer
COD	Autoanalyzer
U	Resin separation and fluorimetry (Dall'Aglio & Casentini, 1970)
Ra	Det. ^{222}Rn in equilibrium by scintillation (Mastino, 1975)
210_{Pb}–210_{Po}	Electrodeposition and alpha spectrometry
Se	APDC-Se extraction in $CHCl_3$, re-extraction and FGSAA (Dall'Aglio *et al.*, 1978)
As	Extraction of AsH_3, concentration of As in Iodine solution and FGSAA (Cremisini *et al.*, 1979)
Fe, Mn	Directly by FGSAA

GLASSWARE

The glassware used is all of Pyrex. All glassware must be suitably washed and purified before use.

REAGENTS

The use of pure reagents for analysis does not always prevent the addition of relatively large quantities of the elements to be analyzed and special purification procedures must be carried out, thus in the case of heavy metals and arsenic analysis for example (Brondi *et al.*, 1981; Cremisini *et al.*, 1979).

Concerning heavy metals all the pyrex test-tubes were treated before using them as follows: first, they were washed with HNO_3 1:4 ratio and then with dithizone in chloroform at pH 9–9.2 value. Finally they were rinsed with distilled deionized water.

Concerning As, the problem was solved by adopting the following purification procedure:

$NaBH_4$ solution: 2 drops of concentrated HCl every 10 ml of solution were added to the $NaBH_4$ solution at 12% freshly prepared.

It was gently shaken and it was ready for use.

HCL: The purified borohydride solution was added to the concentrated HCL in a 1:5 ratio.

At the end of the reaction the HCL resulting was purified from As.

Distilled Deionized Water (DDW), obtained by Milli-Q Reagent-Grade Water System, is always used.

FIELD OPERATIONS

The determinations of the chemical and physical parameters (t°C, pH, Eh, electrical conductance), and of Ca^{2+}, Mg^{2+}, HCO_3^- contents are carried out in the ***field at the sampling site.*** In addition, the sample is filtered with the 500 ml Millipore pressure Kit through a 0.45 μm cellulose acetate filter. The filtered water is placed into highly pure polyethylene bottles, and hydrochloric acid (1 + 1) (ultrapure) is added up to a pH value slightly lower than 2.

At the sampling site, the following solvent extractions are also carried out.

Zn, Cu, Pb and Cd are extracted as dithizonates in chloroform; a 200 ml aliquot of water is put into a 500 ml separatory funnel, the pH value is adjusted to 9.3 by adding approx. 10 ml of buffer solution (141 g of trisodium citrate and 19 g of hydroxilamine hydrochloride with water to 1 l, adjusted to the pH value of 9.3 with 1 + 1 ammonia), and a few drops of 1 + 1 ammonia. 2 ml aliquots of dithizone in chloroform (1 ml = 0.1 – 0.2 μg Zn) are added and the funnel is shaken for 60 sec. This operation is repeated until the endpoint of the colourimetric titration is reached (grey color). The concentration of total heavy metals (Cu + Zn + Pb + Cd) in the sample is expressed as μg Zn/l. After separation, the chloroform containing the heavy metal dithizonates is placed into a 14 ml Pyrex test-tube with a glass stopper for GFAAS elemental analysis in the laboratory.

Mercury is extracted as dithizonate in chloroform; a 500 ml water aliquot is put into a 1000 ml separatory funnel and the pH value is adjusted up to a value slightly less than 2 by adding 1 + 1 HCl; 10–15 ml of hydroxilamine hydrochloride solution (10% w/v) are added and the funnel is shaken.

3 ml of dithizone solution in chloroform are then added and the funnel is shaken for 60 sec. After the chloroform is separated it is put into a Pyrex test-tube and the dithizone solvent extraction is added into the above Pyrex test-tube. 1 ml of 0.01 M HNO_3 containing Au 0.01% w/v and $K_2Cr_2O_7$ 3% w/v is added into the test-tube, which is thereafter stoppered and vigorously shaken for 60 s.

After these operations are accomplished, all the Hg originally present in the 500 ml water aliquot is quantitatively transferred into the 1 ml supernatant aqueous solution, and the stoppered test-tube is finally sent to the laboratory.

To check the conservation of this element in such conditions 10 ng/l, 50 ng/l, 100 ng/l and 1000 ng/l were stored and analyzed weekly.

Within a month any significant loss of this element was found.

Mo, Cr, V, Co and Ni are extracted as APDC-Me complexes in chloroform. A 200 ml water aliquot is put into a 500 ml Pyrex separatory funnel, the pH value is adjusted up to 3.5 4; 0.3 ml of 1% APDC-water w/v solution are added and the funnel shaken for 2 min. 3 ml of chloroform are added and the funnel is shaken for 2 min. The chloroform is separated and put into a 14 ml Pyrex test-tube. The entire extraction is repeated once more and the resulting chloroform extracted is added into the same test-tube, which is sealed and sent to the laboratory.

LABORATORY ANALYSIS:

In the laboratory the analyses listed in Table II are routinely carried out.

All the trace elements considered, apart from U, Rn, Ra and Li, are analyzed by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS), using HGA-72 or HGA-500 provide with Zeeman compensation technique Graphite Furnace and a Mod. 5000 Spectrophotometer, all by Perkin–Elmer.

The operating procedures are as follows.

Zn, Cu, Pb and Cd, already extracted as dithizonate solution in chloroform, and stored in a Pyrex test-tube, are back extracted into diluted acid solution by adding 20 μl of conc. HNO_3 into the test-tube, which is vigorously shaken in order to destroy Me-dithizone complexes. 1 ml of 0.1 M HCl is added and the test-tube vigorously shaken again for 60 secs. At this point all the Heavy Metals originally present in the 200 ml water aliquot are quantitatively transferred into the 1 ml of 0.1 M HCl. 25 μl of this last solution and analyzed in GFAAS for each element. By using the HGA-500 Graphite Furnace and the Mod. 5000 Spectrophotometer the analyses are carried out according to the specifications of Table II.

Mercury. In the laboratory 25 μl of the supernatant aqueous solution in the Pyrex test-tube already prepared in the field are directly used in GFAAS analysis according to the specifications of Table III.

Cr (VI), V, Mo, Co and Ni, already extracted in the field as Me-APDC chelates in chloroform and stored in a Pyrex test-tube, are back acid extracted by adding 20 μl of Br_2 (1 + 1 v/v in chloroform): the test-tube is then vigorously shaken for 60 sec in order to destroy the Me-APDC complex. 1 ml of 0.1 M HCl is then added and the test-tube vigorously shaken again for 60 sec; 25 μl of this last solution, containing the element, originally present in the 200 ml aliquot, is analyzed by GFAAS.

CONCLUSIONS

The advantages obtained by these procedures are essentially the following:

1) In the first place, a greater enrichment factor is obtained as a result of the two extractions in series, hence far lower overall detection limit too.

2) The GFAAS determinations prove to be reliable because there is no matrix variation from one sample to another.

3) Problems regarding transportation and storage of the samples are minimized because the organic solvent extracts prepared in the field are stored and brought to the laboratory. Such extracts have

TABLE III

Operating procedures for trace analysis by GFAAS (Models HGA-500 and 5000, Perkin–Elmer). Fe and Mn are determined starting directly from the acidified water sample, other trace elements starting from the aqueous solution in which element(s) are re-extracted from the organic solvent extracts previously obtained (some times directly in the field). The last step(s)—under the dotted line—are carried out *in order* to clean the Graphite Furnace for the successive run

	Fe	Mn	Cr	V	Mo	Co	Ni	Zn	Cu	Pb	Cd	As	Se	Hg	Al
Wavelength nm	248.3	279.5	357.9	318.4	313.3	240.7	232.0	213.8	324.8	217.0	228.8	193.7	196.0	253.7	309.3
Slit Low, nm	0.2	0.2	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Expansion	×5	×5	×10	×10	×10	×10	×10	×1	×5	×5	×5	×10	×10	×10	×10
STEP 1															
Temp. °C	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
Ramp time	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Hold time	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
STEP 2															
Temp. °C	250	250	250	250	250	250	250	200	200	200	200	200	150	120	250
Ramp time	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Hold time	30	30	30	30	30	30	30	20	20	20	20	20	20	20	30
STEP 3															
Int. flow											50	50		10	
Temp. °C	1200	1200	1200	1200	1200	1200	1200	350	1000	500	2200	1000	300	1200	1200
Ramp time	1	1	1	1	1	1	1	1	1	1	1	5	1	1	1
Hold time	10	10	10	10	10	10	10	10	10	10	5	40	5	5	10
STEP 4															
Int. flow	50	50	10	10	10	10	10		50	50		300	10		10
Temp. °C	2700	2700	2700	2700	2700	2700	2700	2100	2700	2500	2700	200	2600	2700	2700
Ramp time	1	1	1	1	1	1	1	5	1	1	1	1	1	1	1
Hold time	5	5	5	5	5	5	5	5	5	5	3	5	5	3	5
STEP 5															
Int. flow												10			
Temp. °C	2700	2700	2700	200	200	2700	2700	2500	2700	2700		2600	2700		2700
Ramp time	1	1	1	1	1	1	1	1	1	1		1	1		1
Hold time	3	3	3	5	5	3	3	3	3	3		5	3		3
STEP 6															
Temp. °C				2700	2700							2700			
Ramp time				1	1							3			
Hold time				5	5							3			

TABLE IV

Trace element distribution of F, Li, Zn, Cu, Pb, Cd, Cr, As, V, Mo, Hg, Ni e Co in the natural waters of the Latium Region (Italy)

	F	Li	Zn	Cu	Pb	Cd	Cr	As	V	Mo	Hg	Ni	Co
	mg/l							μg/l					
Lago													
BRACCIANO	1.63	32.0	0.23	0.19	0.06	0.01	≤0.004	2.00	0.68	0.26	≤0.003	0.05	0.005
VICO	1.06	22.0	0.09	0.20	0.02	0.01	0.01	15.00	0.35	0.55	≤0.003	0.20	0.006
BOLSENA	1.41	26.0	0.05	0.20	0.02	0.01	0.02	2.40	0.57	0.45	≤0.003	0.14	0.004
TRASIMENO	0.63	1.0	0.05	0.50	0.02	0.01	0.05	0.02	0.22	0.28	≤0.003	0.39	0.007
Sorgente													
PESCHIERA 1	0.10	1.0	0.35	0.26	0.10	0.16	0.16	0.40	0.42	0.54	≤0.01	0.88	0.012
PESCHIERA 2	0.08	1.1	0.25	0.20	0.10	0.16	0.15	0.60	0.43	0.41	≤0.01	0.23	0.005
NINFA	0.08	0.8	0.10	0.23	0.09	0.20	0.17	5.0	0.88	0.22	≤0.01	0.20	0.012
SARDELLANE	0.19	2.2	1.40	1.50	0.06	0.15	0.10	14.60	0.88	0.72	0.05	0.60	0.012
Fiume													
TEVERE (Orte)	0.25	8.5	0.40	0.50	0.15	0.13	0.14	1.40	0.28	0.32	≤0.01	0.93	0.055
TEVERE (P. Galeria)	0.34	14.8	0.75	0.90	0.15	0.13	0.24	8.60	0.32	0.65	≤0.01	2.40	0.190
GARIGLIANO (Foce)	0.19	4.3	0.30	0.65	0.09	0.3	0.10	4.50	0.70	0.85	≤0.01	0.58	0.110

much higher concentrations of the elements to be analyzed than the water sample from which they were obtained.

All the other critical steps have been carefully reviewed in the precedures adopted so as to eliminate, or at least minimize, the risk of adding to or taking away from the sample appreciable quantities of the elements to be analyzed.

These analytical procedures, have been widely applied to the hydrogeochemical study of Italian Inland waters. Among the surveys carried out during the last two years the data collected on the geochemistry of natural waters of Latium Region are presented because of the peculiar interest of this Region from a geological and hydrogeochemical point of view (Table IV). The conclusions which can be drawn from this survey can be summarized as follows.

1. Some large water bodies show an extremely low content of many trace elements, much lower than those given till now for the same or similar water bodies. Notice particularly the extremely low content of Zn, Cr, Cd, Pb and Hg in Bracciano and Bolsena lakes. These unexpected results indicate that, from one side, the analytical procedures adopted do not contaminate the water sample and, on the other side, that these lakes and springs do not show any kind of trace element pollution.

2. Some natural processes such as the leaching of volcanites or hydrothermal circulation are responsible for relatively high levels of elements like V, As and Hg. Notice particularly the high As content in Bracciano, Vico and Bolsena lakes and in Anguillara and Sardellane springs (respectively 2.0, 15, 2.4, 19 and 15 μg/l).

3. Advanced statistical processing is very useful in aiding the geochemist in understanding the processes actually acting in the area under investigation, but the automatic data processing alone is an incomplete explanation of all the processes taking place.

Mercury distribution in natural waters of the Latium Region shows a peculiar pattern in the sense that the contents higher than the normal ones seem to depend on an hydrothermal input; the carried out factor analysis does not help at all in interpreting these results.

4. The first necessary step, towards an accurate evaluation of the man-induced alteration of the trace element levels in natural waters

is a comprehensive study of their natural levels under the various possible geochemical conditions.

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