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Determination of major and trace elements in European bottled mineral water — Analytical methods

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A B S T R A C T

A total of 1785 European bottled water samples were analyzed using standard laboratory methods. The bottled water samples were purchased in 2008 at supermarkets throughout 40 European countries. The samples were analyzed for 71 chemical parameters (As, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br^-, HCO_3^-, Cl^-, F^-, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, SiO_2, pH, and EC) by quadrupole inductively coupled emission spectroscopy (ICP-QMS, trace elements), inductively coupled plasma atomic emission spectroscopy (ICP-AES, major elements), ion chromatography (IC, anions), atomic fluorescence spectrometry (AFS, Hg), titration (alkalinity), photometric methods (NH_4^+), potentiometric methods (pH), and conductometric methods (specific electrical conductivity, EC). A very strict quality control procedure was followed by analysing blanks, international reference materials, an internal project standard, and duplicate analyses, as well as by analysing 23 elements by both ICP-QMS and ICP-AES. Analysis of marketed bottled water from springs, wells or boreholes, apart from the evaluation of its quality with respect to inorganic elements, it may provide a cheap alternative to obtain a first impression about groundwater chemistry at the European scale.

1. Introduction

Over the last 20 years, bottled mineral water has gained in popularity and sales volume has risen rapidly worldwide. The European Groundwater Geochemistry Project was conducted by the EGS Geochemistry Expert Group to show that bottled mineral water can provide important information about the geological subsurface. Bottled mineral water is essentially pure groundwater and is sold in supermarkets all over Europe, and is thus readily available for sampling and analysis.

In the EU countries, there are more than 1230 brands recognized by the EU (EU, European Union, 2005). For this study, 1785 bottled water samples were purchased, including duplicated bottles of the same brand, but bought from different supermarkets, and when a particular brand was packed in glass and plastic bottles, both packages were obtained. These bottled water samples represent 1247 individual springs, wells or boreholes, and come from 884 localities.

In many countries there are regulations specifically governing the sale of bottled mineral water. In the European Community, directives 1980/777/EEC (1980a), 1996/70/EC (1996) and 2003/40/EC (2003) state that bottled water must be definitely groundwater, and clearly distinguishable from ordinary drinking water by its nature. The EU has passed regulations for action levels for trace elements in drinking and bottled water (EU Directive 1980/778/EEC, 1980b; EU Directive 1998/83/EC, 1998; EU Directive 2003/40/EC, 2003). International standards have also been set by WHO (1996, 2006), and FAO (1997).

Water is essential for life and an important source of intake of trace elements by humans. The consumption growth rate for bottled water is higher than that of all beverage sectors. According to Datamonitor (2008) in terms of sales the global bottled water market grew by 7% in 2006 to reach a value of US$60,938.1 million, whereas the market value for 2011 is forecast to be in the order of $86,421.2 million, an increase by 41.8% since 2006. With respect to volume, the market grew by 8.1% in 2006 to reach a volume of 115,393.5 million litres, and the global market forecast for 2011 is estimated to require a volume of 174,286.6 million litres, an increase by 51% since 2006. European countries, comprising Belgium, the Czech Republic, Denmark, France, Germany, Hungary, Italy, Netherlands, Norway, Poland, Russia, Spain, Sweden and the UK, is the leading region in bottled water sales, holding a 52.9% share of the global market. Therefore, apart from the novel use of bottled water as a first estimate

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of groundwater geochemistry, the public in general is interested to know its quality.

Many studies have demonstrated that water can be severely contaminated by the storage bottles (Moody and Lindstrom, 1977; Laxen and Harrison, 1981; Benoit et al., 1997; Hall, 1998; Reimann et al., 1999, 2007). For example, Pb is leached from glass bottles, and many PET (polyethylene terephthalate) bottles contaminate the water with Sb (Shotyk et al., 2006; Shotyk and Krachler, 2007a, b; Krachler and Shotyk, 2009).

Analytical methods capable of detecting low concentrations are necessary for determining trace elements in drinking water (bottled mineral and tap water). With the introduction of commercially available inductively coupled plasma mass spectrometers (ICP-MS) in 1983, element analysis gained a powerful tool, and has now become the method of choice for the analysis of water (Allen et al., 1989, 1991; Moens and Jakubowski, 1998; Giessmann and Greb, 1994; Riondato et al., 2000; Banks et al., 1999; Reimann et al., 1996; Hall et al., 1996; Gäbler, 2002).

Double focusing sector field ICP-MS and quadrupole ICP-MS enable direct determination of elements of interest with no preconcentration or separation required (Riondato et al., 2000).

Besides being able to simultaneously analyze many elements, quadrupole ICP-MS also offers high sensitivity over a wide linear range and low detection limits. Most commercially available ICP-MS instruments have quadrupole mass filters. An alternative approach for mass separation is the use of magnetic sector mass spectrometers (Bradshaw et al., 1989; Gäbler, 2002).

Generally, ICP-MS has been accepted as an instrumental technique that provides rapid and sensitive multielement analysis of liquid and solid samples.

2. Materials

For this study, 1785 bottled water samples, purchased from November 2007 to April 2008 at supermarkets from 40 European countries, were analyzed for 71 parameters. Prior to analysis all bottled water samples were stored in refrigerators at the BGR laboratories. Additionally, 579 tap water samples from 29 European countries were analyzed, and the results compared with those of bottled water, European stream water (Salminen et al., 2005) and Norwegian groundwater by plotting the four datasets on cumulative probability plots (EGS, EuroGeoSurveys Geochemistry Expert Group, 2010).

3. Laboratories and instrumentation

The bottled mineral water samples were analyzed by ICP-AES, ICP-QMS, IC, titration and photometric methods in the laboratories of the BGR (Table 1).

After adjusting the bottled water to room temperature, pH (SenTix 81, glass electrode) and electrical conductivity (WTW TetraCon 325) were measured (WTW Multiline P4 electrode) with a precision of 0.01 for both parameters.

3.1. ICP-QMS analyses

Sample preparation (acidification and transfer to polypropylene (PP) tubes) and the ICP-QMS analysis were carried out using clean room procedures (class 10,000 clean room) in the BGR laboratories. Disposable polyethylene (PE) gloves (all other gloves contain heavy metals, e.g. Zn) were used for all work in the clean room.

The samples were analyzed by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) using an Agilent 7500ce instrument. The instrument is equipped with a standard peristaltic pump, a Micro Mist concentric nebulizer, a Peltier-cooled spray chamber, the Plasma Forward Power, the Shield Torch System, and a Collision/Reaction Cell system. An autosampler (ASX 520, Cetac Technologies) was employed to introduce the analytes into the plasma of the ICP-MS. Sample introduction was done with a Micro Mist concentric nebulizer and Scott-type quartz glass spray chamber.

Details of the instrument settings and scanning conditions are tabulated in Table 2. The analyses were conducted according to the German norm DIN 38406-29 (1996).

Hydrogen was considered to be useful as a reaction gas only for Se. Helium was used as the collision gas for Ag, As, Co, Cr, Cu, Fe, Ga, Ge, Mo, Ni, Sc, Ti and Zn. No cell gas was used for the other elements.

Normally the analysis of iodine by ICP-MS requires special sample treatment and elimination of polyatomic interferences, in addition to keeping iodine in solution. But, for bottled water, which has weakly acidic to acid pH, iodine can be measured directly.

For the determination of iodine in this study, however, the samples were acidified with 1% ultrapure HNO_3. The instrument was calibrated with iodate. It was also attempted to stabilize iodine at basic pH, but the measurements were not reproducible.

Within the framework of the Geochemical Atlas of Germany (Birke et al., 2006), ten water samples from different sources were acidified with 1% ultrapure HNO_3, and stored in fluorinated ethylene propylene (FEP) bottles for three years at low temperature (<4 °C) and measured at different times. The measured iodine concentrations were reproducible over the entire three years. It has been reported that acidification can result, however, in the formation of elementary iodine, which can be adsorbed on the bottle walls and instrument tubing. But it has been verified that when HNO_3 is used for acidification, the iodine is oxidized to the iodate; this can occur at different rates and for this reason there are no commercial certified standards for iodine. The mass spectrometer measurements were made on ^{127}I. Bottled water samples with high iodine concentrations were immediately reanalyzed at several dilutions to test the stability of the measurement. After the measurement of a high iodine concentration, the water samples were reanalyzed using the following procedure in order to exclude the possibility of a memory effect. A newly cleaned sample input system (tubing, sampler and skimmer cones, spray chamber) was used for each measurement. Each PP tube was used only once.

It is known that interference corrections must be used for the numerous overlaps of the various REE oxides. The collision cell conditions that were used cannot eliminate these overlaps. A correction algorithm similar to that of Hall et al. (1995, 1996) was used to correct for the influence of BaO on the peaks for ^{151}Eu and ^{153}Eu. The correction was made for each individual analytical sample batch to take into consideration the rate of BaO formation (0.8–1.0%). Appropriate settings for the Agilent spectrometer were selected, so that REE oxide formation was minimized. It is known that many of the REEs require 3–4 such corrections in order to obtain accurate results.

3.2. ICP-AES analyses

The acidified and non-acidified water samples were analyzed using an ICP-AES (a Spectro Ciros instrument) with radial plasma measurement according to DIN EN ISO 11885 (1998). The wavelengths and detection limits are given in Table 3 for the analyzed elements. The detection limits were estimated from the calibration curves according to DIN 32645 (1994).

Blank samples (0.15 M HNO_3 in deionized water) were measured for calibration of the instrument. A multielement standard solution containing the elements of Table 3 in 0.15 M HNO_3 was also used. This standard of known composition was analyzed as part of each batch of samples.

3.3. Ion chromatography (IC)

A Dionex ICS 3000 ion chromatograph, equipped with a conductivity detector, an AS 19 column and a self-regenerating suppressor using a KOH eluent, was used for the determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-

Table 1
Analytical methods, detection limits and precision at the 95% confidence level.

Parameter	Unit	Analytical method	Isotope	Used gases	Instrument detection limit (IDL)	Reported detection limit (RDL)	Practical detection limit (PDL)	Precision (%)
pH		Potentiometric		–	–	–	–	–
EC	µS/cm	Conductometric		–	–	–	–	–
Ag	µg/L	ICP-QMS	Min: 107–109	He GM[a]	0.001	0.002	0.002	13
Al	µg/L	ICP-QMS	27	NGM[b]	0.2	0.5	0.2	5
As	µg/L	ICP-QMS	75	He GM[a]	0.01	0.03	0.001	10
B	µg/L	ICP-QMS	11	NGM[b]	0.1	2.0	0.2	4
Ba	µg/L	ICP-QMS	137	NGM[b]	0.005	0.1	0.2	5
Be	µg/L	ICP-QMS	9	NGM[b]	0.001	0.01	0.005	5
Bi	µg/L	ICP-QMS	209	NGM[b]	0.0005	0.005	0.003	–[d]
Ca	mg/L	ICP-AES		–	0.005	0.01	–	–
Cd	µg/L	ICP-QMS	114_cor	NGM[b]	0.001	0.003	0.002	29
Ce	µg/L	ICP-QMS	140	NGM[b]	0.0005	0.001	0.0001	13
Co	µg/L	ICP-QMS	59	He GM[a]	0.002	0.01	0.002	5
Cr	µg/L	ICP-QMS	52	He GM[a]	0.01	0.2	0.014	7
Cs	µg/L	ICP-QMS	133	NGM[b]	0.0005	0.002	0.004[c]	3
Cu	µg/L	ICP-QMS	Min: 63–65	He GM[a]	0.01	0.1	0.029	2
Dy	µg/L	ICP-QMS	163	NGM[b]	0.0002	0.001	0.001	16
Er	µg/L	ICP-QMS	166	NGM[b]	0.0002	0.001	0.0004	13
Eu	µg/L	ICP-QMS	151_kor	NGM[b]	0.0002	0.001	0.001	18
Fe	µg/L	ICP-QMS	56	He GM[a]	0.01	0.5	0.08	4
Ga	µg/L	ICP-QMS	71	He GM[a]	0.0005	0.005	0.005	4
Gd	µg/L	ICP-QMS	157	NGM[b]	0.0002	0.002	0.001	22
Ge	µg/L	ICP-QMS	72	He GM[a]	0.005	0.03	0.02	6
Hf	µg/L	ICP-QMS	178	NGM[b]	0.0001	0.002	0.001	28
Hg	ng/L	AFS		–	1.0	5.0	–	–
Ho	µg/L	ICP-QMS	165	NGM[b]	0.0001	0.001	0.0003	19
I	µg/L	ICP-QMS	127	NGM[b]	0.01	0.2	0.09	15
K	mg/L	ICP-AES		–	0.05	0.1	–	–
La	µg/L	ICP-QMS	139	NGM[b]	0.0001	0.001	0.001	9
Li	µg/L	ICP-QMS	7	NGM[b]	0.01	0.2	0.14	5
Lu	µg/L	ICP-QMS	175	NGM[b]	0.00005	0.001	0.0002	16
Mg	mg/L	ICP-AES		–	0.005	0.01	–	–
Mn	µg/L	ICP-QMS	55	NGM[b]	0.005	0.1	0.111	2
Mo	µg/L	ICP-QMS	95	He GM[a]	0.001	0.02	0.017	4
Na	mg/L	ICP-AES		–	0.02	0.1	–	–
Nb	µg/L	ICP-QMS	93	NGM[b]	0.001	0.01	0.001	15
Nd	µg/L	ICP-QMS	146	NGM[b]	0.0001	0.001	0.001	18
Ni	µg/L	ICP-QMS	60	He GM[a]	0.005	0.02	0.01	4
Pb	µg/L	ICP-QMS	Sum: 206 + 207 + 208	NGM[b]	0.001	0.01	0.003	6
Pr	µg/L	ICP-QMS	141	NGM[b]	0.00005	0.001	0.0002	15
Rb	µg/L	ICP-QMS	85	NGM[b]	0.001	0.01	0.30[c]	6
Sb	µg/L	ICP-QMS	121	NGM[b]	0.001	0.01	0.0001	6
Sc	µg/L	ICP-QMS	45	He GM[a]	0.001	0.02	0.001	23
Se	µg/L	ICP-QMS	78	H_2 GM[e]	0.005	0.02	0.009	19
Sm	µg/L	ICP-QMS	147	NGM[b]	0.0001	0.001	0.001	23
Sn	µg/L	ICP-QMS	118	NGM[b]	0.001	0.02	0.003	12
Sr	mg/L	ICP-AES		NGM[b]	0.001	0.001	–	–
Ta	µg/L	ICP-QMS	181	NGM[b]	0.0005	0.005	0.002	–[d]
Tb	µg/L	ICP-QMS	159	NGM[b]	0.00005	0.001	0.0002	23
Te	µg/L	ICP-QMS	126	NGM[b]	0.001	0.03	0.01	–[d]
Th	µg/L	ICP-QMS	232	NGM[b]	0.0001	0.001	0.0004	33
Ti	µg/L	ICP-QMS	Min: 47–49	He GM[a]	0.005	0.08	0.04	52
Tl	µg/L	ICP-QMS	205	NGM[b]	0.0005	0.002	0.001	6
Tm	µg/L	ICP-QMS	169	NGM[b]	0.00005	0.001	0.0002	22
U	µg/L	ICP-QMS	238	NGM[b]	0.00005	0.001	0.006[c]	2
V	µg/L	ICP-QMS	51	NGM[b]	0.01	0.1	0.02	6
W	µg/L	ICP-QMS	182	NGM[b]	0.002	0.05	0.009	1
Y	µg/L	ICP-QMS	89	NGM[b]	0.00005	0.001	0.002	7
Yb	µg/L	ICP-QMS	172	NGM[b]	0.0001	0.001	0.001	17
Zn	µg/L	ICP-QMS	Min: 66–68	He GM[a]	0.01	0.2	0.11	3
Zr	µg/L	ICP-QMS	90	NGM[b]	0.0001	0.001	0.013	7
Br^-	mg/L	IC		–	0.003	0.003	–	–
$HCO3^-$	mg/L	Titration		–	2.0	2.0	–	–
Alkalinity	mg/L	Titration		–	0.1	0.1	–	–
Cl^-	mg/L	IC		–	0.01	0.01	–	–
F^-	mg/L	IC		–	0.003	0.003	–	–
NH_4^+	mg/L	Photometric		–	0.005	0.005	–	–
NO_2^-	mg/L	IC		–	0.005	0.005–0.1[f]	–	–
NO_3^-	mg/L	IC		–	0.01	0.01–1.0[f]	–	–

(continued on next page)

Table 1 *(continued)*

Parameter	Unit	Analytical method	Isotope	Used gases	Instrument detection limit (IDL)	Reported detection limit (RDL)	Practical detection limit (PDL)	Precision (%)
PO_4^{3-}	mg/L	ICP-AES		–	0.02	0.02	–	–
P	mg/L	ICP-AES		–	0.01	0.01	–	–
SO_4^{2-}	mg/L	IC		–	0.01	0.01	–	–
SiO_2	mg/L	ICP-AES		–	0.05	0.05	–	–
Si	mg/L	ICP-AES		–	0.03	0.03	–	–

[a] He gas mode.
[b] No gas mode.
[c] Too large concentration range and too many high values to reliably calculate PDL.
[d] Insufficient values above detection to estimate precision.
[e] H_2 gas mode.
[f] Dependent on TDS.

and SO_4^{2-} in nonacidified water samples, according to DIN EN ISO 10304-1 (1995). The detection limits of this method are given in Table 1.

3.4. Photometric analyses

Ammonium ion was analyzed photometrically using a Thermo Unicam UV 300 spectrometer according to DIN 38406-5 (1983) in samples that were not acidified. The detection limits estimated from the calibration curve, and calculated according to DIN 32645 (1994), are tabulated in Table 1.

3.5. Titration method

The alkalinity was determined on nonacidified bottled water samples by titration with 0.05 M HCl. This was done with an automatic Metrohm titrator on a 50 mL water sample. The titration result is given as bicarbonate concentration (titration end point 4.3 in acid pH range) or carbonate (titration end point 8.2 in weakly basic pH range). The detection limit is 1 mg HCO_3^-/L.

3.6. Atomic fluorescence spectrometry (AFS)

Atomic fluorescence spectrometry was used for the determination of mercury (Instrument PSA 10.035 Millennium Merlin 1631).

Elemental mercury vapor is generated from the sample by reduction with tin(II) chloride, and is purged from the solution by an argon carrier stream. The mercury vapor is detected by atomic fluorescence spectrometry.

The system uses continuous flow vapor generation, the mercury vapor is passed over a gold trap where the mercury is concentrated. After collection for a set time, the mercury is then thermally desorbed into the atomic fluorescence detector.

The sample is stabilized by a mixture of potassium dichromate and nitric acid (5 g potassium dichromate in 1 L HNO_3 (64%), 1 mL in 100 mL sample).

The linear dynamic range of this method is approximately 0.1 ng Hg/L to 100 µg Hg/L.

Accuracy and precision were controlled continuously by using CRMs (Certified Reference Materials) BCR 60 and BCR 61.

High purity MERCK reagents (SUPRAPUR) are used in all cases; prior to use, the tin(II) solution is purged for 24 h with nitrogen.

4. Laboratory procedure

The mineral water bottles were stored in laboratory refrigerators prior to analysis. About 3000 new 250 mL HDPE (high-density polyethylene) bottles and LDPE (low-density polyethylene) screw caps, as well as 3000 125 mL FLPE (fluorinated high-density polyethylene) bottles and PP (polypropylene) screw caps were procured for the project.

Table 2
Instrument settings and scanning conditions of the Agilent 7500ce (ICP-QMS).

Tuning parameters	
Plasma forward power	1550 W
Reflected power	1 W
Sampling depth	8 mm
Cool gas flow	15.0 L/min
Carrier gas flow	0.72 L/min
Makeup gas flow	0.28 L/min
He collision gas flow	5.1 mL/min He 5.3
H_2 reaction gas flow	4.2 mL/min H_2 5.3
Spray chamber	Scott/Duran
Spray chamber temp	10 °C
Nebulizer	MicroMist
Sample uptake	0.4 mL/min
Oxide CeO156/Ce140	0.8–1.0%
Doubly charged Ce140/70	1–3%
Acquisition parameters	
Points per mass	1
Repetitions	3
Scans/repetition	100
Stabilization sample	60 s
Stabilization no gas	15 s
Stabilization H_2	15 s
Stabilization He	15 s
Total acquisition time	165 s
Rinse time (intelligent) for Sb, Tl, U	30–90 s

Table 3
Wavelengths and instrument detection limits for elements analyzed by ICP-AES.

Element	Wavelength (nm)	Instrument detection limit (mg/L)
Al	167.078	0.003
B	249.678	0.01 as BO_2
Ba	455.404	0.0005
Be	313.042	0.0005
Ca	317.933, 422.673	0.005
Cd	228.802	0.002
Co	228.616	0.003
Cr	267.716	0.003
Cu	324.754	0.003
Fe	259.94	0.003
K	766.49	0.05
Li	670.78	0.003
Mg	285.213, 279.079	0.005
Mn	257.611	0.001
Na	589.592	0.02
Ni	231.603	0.005
P	177.49	0.01 as PO_4^{3-}
Pb	220.351	0.02
Sc	361.364	0.001
Si	251.611	0.03 as SiO_2
Sr	407.771	0.0003
V	311.071	0.003
Zn	213.856	0.003

Table 4
Analytical results (in µg/L) for standard samples repeatedly analyzed by ICP-QMS over entire period that measurements were made (SLSR-4, TM26.3, TM-27.2).

	SLSR-4[a] (n = 103)				TM-26.3[b] (n = 26)			TM-27.2[b] (n = 25)			
	Mean	cert.-val.[c]	publ.-val.[d]	CV (%)[e]	Mean	cert.-val.[c]	CV (%)[e]	Mean	cert.-val.[c]	publ.-val.[d]	CV (%)[e]
Ag	< 0.001	–	0.035	(30.2)	6.75	6.9	3.95	1.34	–	1.0	9.79
Al	53.2	54	53.5	4.68	67.9	69	6.30	14.9	14.5	14.5–15	9.44
As	0.69	0.68	0.68–0.7	3.62	7.64	7.9	4.20	2.35	2.4	2.4	5.01
B	5.7	–	5.7–6.3	13.6	36.0	36	4.31	–	–	–	–
Ba	12.8	12.2	12.2–12.6	2.09	24.8	25	2.67	5.20	5.1	5.1	3.63
Be	0.007	0.007	0.007	17.2	3.28	3.4	4.85	1.38	1.4	1.4	5.50
Bi	0.0029	–	0.0022	20.3	4.43	3.3	2.96	1.71	–	1.5	3.48
Br	35.1	–	47.8	6.76	–	–	–	–	–	–	–
Ca	5350	6200	5200–6200	2.97	–	–	–	–	–	–	–
Cd	0.013	0.012	0.012	12.5	7.04	7.1	3.25	1.23	1.2	1.2	3.93
Ce	0.367	–	0.360	2.10	–	–	–	–	–	–	–
Co	0.037	0.033	0.033–0.048	12.8	8.08	8.1	3.87	2.37	2.3	2.3	4.73
Cr	0.342	0.33	0.312	13.0	11.8	12.3	4.56	1.84	1.8	1.8–1.9	5.50
Cs	0.007	–	0.007–0.009	11.1	–	–	–	–	–	–	–
Cu	1.80	1.81	1.86	3.93	12.9	13.4	3.89	4.77	4.6	4.6	3.97
Dy	0.0238	–	0.0242	4.82	–	–	–	–	–	–	–
Er	0.0136	–	0.0134	5.99	–	–	–	–	–	–	–
Eu	0.009	–	0.008	6.76	–	–	–	–	–	–	–
Fe	102	103	95–117	4.30	22.2	21	4.02	11.8	11.4	11.4	4.44
Ga	0.021	–	0.012	33.1	4.86	5.4	3.79	–	–	–	–
Gd	0.0385	–	0.0342	5.35	–	–	–	–	–	–	–
Ge	0.022	–	0.010	17.9	–	–	–	–	–	–	–
Hf	0.0039	–	0.0033	30.9	–	–	–	–	–	–	–
Ho	0.0049	–	0.0047	6.39	–	–	–	–	–	–	–
K	540	680	597–712	12.2	–	–	–	–	–	–	–
La	0.292	0.287	0.287	2.24	–	–	–	–	–	–	–
Li	0.51	–	0.54	11.7	6.26	6.6	5.85	3.87	3.9	3.9	6.13
Lu	0.0020	–	0.0019	8.48	–	–	–	–	–	–	–
Mg	1530	1600	1600–1624	3.61	–	–	–	–	–	–	–
Mn	3.38	3.37	3.37	3.67	16.9	17.0	4.55	2.64	2.6	2.6	4.70
Mo	0.21	0.21	0.21	5.90	7.77	7.6	2.93	2.55	2.4	2.4	3.04
Na	2110	2400	2400–2500	5.68	–	–	–	–	–	–	–
Nb	0.0068	–	0.0041	63.7	–	–	–	–	–	–	–
Nd	0.267	–	0.269	2.68	–	–	–	–	–	–	–
Ni	0.73	0.67	0.67–0.82	11.3	10.1	10.2	3.81	2.66	2.6	2.5–2.6	5.42
Pb	0.088	0.086	0.084–0.086	17.4	10.6	10.5	2.61	3.27	3.2	3.2	3.18
Pr	0.0695	–	0.0693	2.33	–	–	–	–	–	–	–
Rb	1.53	–	1.53	2.65	9.99	10	3.67	–	–	–	–
Sb	0.25	0.23	0.23–0.27	3.19	2.59	2.7	2.90	1.82	1.9	1.9	2.61
Sc	0.029	–	0.011–0.05	29.6	–	–	–	–	–	–	–
Se	0.09	–	0,23	12.2	4.93	5.6	4.40	1.30	1.6	1.6	5.75
Sm	0.059	–	0.0574	4.93	–	–	–	–	–	–	–
Sn	0.021	–	0.008–0.010	37.6	6.14	5.9	2.31	2.82	–	2.6	2.69
Sr	26.5	26.3	26.3–28.2	2.82	90.3	96	4.05	51.0	54.4	54.4	4.65
Ta	0.0023	–	0.0003	126	–	–	–	–	–	–	–
Tb	0.0046	–	0.0043	5.54	–	–	–	–	–	–	–
Te	0.008	–	0.004	49.3	–	–	–	–	–	–	–
Th	0.0201	–	0.019–0.022	6.90	–	–	–	–	–	–	–
Ti	1.04	–	1.31–1.56	17.2	5.16	6.0	11.3	2.06	2.4	2.4	12.8
Tl	0.0087	–	0.0076	49.8	4.91	5.2	4.85	1.73	1.8	1.8	4.84
Tm	0.0019	–	0.0017	8.58	–	–	–	–	–	–	–
U	0.049	0.050	0.047–0.053	3.63	7.78	7.5	3.48	2.08	2.0	2.0	3.52
V	0.38	0.32	0.32–0.35	16.1	11.8	12.1	4.23	2.47	2.4	2.4	5.80
W	0.016	–	0.013	83.8	9.65	8.4	4.91	–	–	–	–
Y	0.139	–	0.146	3.07	–	–	–	–	–	–	–
Yb	0.0122	–	0.0120	7.01	–	–	–	–	–	–	–
Zn	1.17	0.93	0.93–1.24	22.1	37.2	39	3.63	13.7	–	14.1	3.79
Zr	0.097	–	0.12	4.96	–	–	–	–	–	–	–

[a] SLSR-4: National Research Council Canada River Water Reference Material for Trace Metals.

[b] TM-26.3, TM-27.2: National Water Research Institute of Canada fortified standards for trace elements.

[c] cert.-val.: certified reference value.

[d] publ.-val.: published value (http://georem.mpch-mainz.gwdg.de/).

[e] CV (%): coefficient of variation in percent.

The 250 mL HDPE and the 125 mL FLPE bottles and their screw caps were rinsed twice with deionized water (SERALPUR-90, 18.2 MΩ). The 250 mL HDPE bottles were then filled with deionized water and closed with the LDPE screw caps. The filled bottles were then stored on their sides for about four weeks, and the bottles were subsequently emptied before being filled with bottled mineral water.

The 125 mL FLPE bottles were filled with deionized water to which 2 mL of 69% HNO_3 (Roth Suprapure, density 1.41 kg/L) were added; the bottles were then closed with the PP screw caps. These filled bottles were also stored for about four weeks. The bottles were emptied and rinsed twice with deionized water before being filled with bottled mineral water.

Table 5
Analytical results (in µg/L) for standard samples repeatedly analyzed by ICP-QMS over entire period that measurements were made (TM-28.2, TM-28.3, MinWas).

	TM-28.2[a] (n = 38)				TM-28.3[a] (n = 91)			MinWas[b] (n = 261)	
	Mean	cert.-val.[c]	publ.-val.[d]	CV (%)[e]	Mean	cert.-val.[c]	CV (%)[e]	Mean	CV (%)[e]
Ag	3.84	3.30	3.3	8.95	3.68	3.79	3.21	0.915	4.06
Al	47.1	47.0	47–48	5.73	50.0	51.3	5.91	4.84	9.92
As	5.76	5.80	5.8	3.72	5.90	6.22	3.66	9.56	4.51
B	–	–	–	–	12.0	10.4	17.3	37.5	13.6
Ba	16.0	15.7	15.6–15.7	2.88	15.2	15.5	2.66	34.9	3.50
Be	2.36	2.5	2.5	5.67	3.04	3.34	4.25	8.38	4.25
Bi	3.87	3	3.0	2.92	3.16	2.51	3.20	0.973	3.48
Br	–	–	–	–	–	–	–	30.9	9.16
Ca	6980	7400	7400	3.98	–	–	–	78,300	4.82
Cd	1.34	1.3	1.3	3.01	1.88	1.91	3.06	0.977	3.85
Ce	–	–	–	–	–	–	–	0.014	5.66
Co	3.67	3.6	3.6	2.91	3.43	3.53	3.50	0.922	4.92
Cr	4.71	4.7	4.7	3.67	4.67	4.83	3.64	1.17	4.95
Cs	–	–	–	–	–	–	–	0.011	18.1
Cu	6.40	6.2	6.2–6.3	3.75	6.02	6.15	3.34	1.39	5.24
Dy	–	–	–	–	–	–	–	0.0038	13.4
Er	–	–	–	–	–	–	–	0.0030	12.7
Eu	–	–	–	–	–	–	–	0.0027	13.4
Fe	18.2	–	17	3.12	17.3	16.5	4.06	11.2	4.40
Ga	–	–	–	–	–	–	–	0.885	7.20
Gd	–	–	–	–	–	–	–	0.0035	17.3
Ge	–	–	–	–	–	–	–	0.010	23.9
Hf	–	–	–	–	–	–	–	< 0.0005	(52.8)
Hg	–	–	–	–	–	–	–	< 5	–
Ho	–	–	–	–	–	–	–	0.0013	16.3
I	–	–	–	–	–	–	–	2.6	21.5
K	316	400	400	8.19	–	–	–	1020	9.42
La	–	–	–	–	–	–	–	0.0109	5.18
Li	3.43	3.6	3.6	6.88	3.77	4.12	6.85	7.93	6.77
Lu	–	–	–	–	–	–	–	0.0005	16.3
Mg	1730	1700	1700	3.58	–	–	–	14,900	4.64
Mn	7.34	7.1	7.1–7.2	3.92	6.87	6.9	4.13	1.05	6.24
Mo	4.27	4.1	4.1	4.01	3.77	3.82	4.30	1.28	5.23
Na	3030	2900	2900	4.16	–	–	–	9600	5.13
Nb	–	–	–	–	–	–	–	0.002	53.4
Nd	–	–	–	–	–	–	–	0.0110	9.84
Ni	11.2	11.1	11.1–11.2	3.63	9.57	9.8	4.24	1.14	6.89
Pb	4.19	4.1	4.1	2.33	4.02	3.97	2.64	1.07	3.05
Pr	–	–	–	–	–	–	–	0.0024	8.24
Rb	–	–	–	–	0.412	0.42	3.47	2.00	3.68
Sb	2.97	3.1	2.8–3.0	3.57	3.15	3.38	3.59	0.070	6.11
Sc	–	–	–	–	–	–	–	0.058	28.8
Se	3.04	3.6	3.6	3.91	3.87	4.31	4.75	9.63	5.62
Sm	–	–	–	–	–	–	–	0.0028	20.5
Sn	–	–	–	–	3.76	3.83	3.49	0.016	144
Sr	48.1	50.8	50.5–50.8	3.91	64.8	69.7	3.81	1220	3.84
Ta	–	–	–	–	–	–	–	< 0.001	(54.8)
Tb	–	–	–	–	–	–	–	0.0005	17.7
Te	–	–	–	–	–	–	–	0.960	6.11
Th	–	–	–	–	–	–	–	0.0020	30.1
Ti	–	–	–	–	7.19	8.1	9.72	0.061	73.0
Tl	3.60	3.7	3.7	2.77	3.73	3.89	3.11	0.969	3.46
Tm	–	–	–	–	–	–	–	0.0005	19.9
U	6.08	5.7	5.7	3.54	6.14	6	3.05	1.52	3.50
V	2.49	2.5	2.5	3.44	2.96	3.07	4.06	1.14	5.78
W	–	–	–	–	–	–	–	0.022	77.7
Y	–	–	–	–	–	–	–	0.0471	5.54
Yb	–	–	–	–	–	–	–	0.0030	15.7
Zn	28.2	22	22	3.22	26.8	27.5	3.63	21.0	4.45
Zr	–	–	–	–	–	–	–	0.024	10.2

[a] TM-26.3, TM-27.2, TM-28.2, TM-28.3: National Water Research Institute of Canada fortified standards for trace elements.
[b] MinWas: in-house project standard.
[c] cert.-val.: certified reference value.
[d] publ.-val.: published value (http://georem.mpch-mainz.gwdg.de/).
[e] CV (%): coefficient of variation in percent.

The mineral water bottles were opened in the laboratory (clean room class 10,000). A 100 mL beaker was filled with mineral water and the electrical conductivity and pH of the mineral water were measured.

The cap was then loosely replaced on the mineral water bottle, and the bottle was degassed for about 20 min in an ultrasound bath. After degassing, 25 mL was withdrawn from the mineral water bottle for the bicarbonate titration. The 250 mL HDPE bottles were then filled with degassed mineral water, and the anions determined by ion chromatography and ammonium ion by titration with HCl. The degassed bottled water was used to first rinse and then fill a 125 mL FLPE bottle.

In the clean room, the water samples were then acidified with 1.5 mL 69% HNO_3 (Roth Ultrapure, density 1.41 kg/L) and shaken.

Table 6
Analytical results (ICP-AES, in mg/L) for the internal laboratory standard samples analyzed repeatedly over entire period that measurements were made.

	CalStd[a] (n = 57)	
	Mean	CV (%)[b]
Ag	0.0366	14.8
Al	0.259	7.44
As	0.200	2.61
Ba	0.140	1.89
Be	0.0990	1.70
Br[c]	0.560	18.7
Ca[c]	219	2.85
Cd	0.103	2.10
Cl[c]	46.6	2.53
Co	0.194	2.00
Cr	0.0951	3.42
Cu	0.107	2.34
Fe	0.112	2.30
K[c]	10.7	1.95
Li	0.146	2.32
Mg[c]	6.93	1.95
Mn	0.107	2.29
Na[c]	41.2	3.25
Ni	0.198	2.29
Pb	0.195	3.16
Sc	0.103	1.96
Sr[c]	1.37	1.86
Ti	0.110	1.93
V	0.0990	2.19
Zn	0.118	2.48
BO_2^-[c]	2.04	2.35
PO_4^{3-}[c]	0.118	12.2
SO_4^{2-}[c]	267	1.24
SiO_2[c]	11.3	2.00

[a] Calibration standard.
[b] CV (%): coefficient of variation in percent.
[c] Used analytical data.

Trace elements were determined by ICP-QMS, and the major cations were also determined by ICP-AES. The ICP-QMS analyses were performed by using 13 mL PP tubes (Sarstedt) with LDPE stoppers. The tubes were filled with 1% suprapure HNO_3 for about four weeks before use, and during this time were often shaken. The tubes were then emptied, rinsed with the sample solution before being filled with the sample aliquot for analysis. Each PP tube was used for only one analysis.

The bottled water samples had to be transferred to the HDPE and FLPE bottles and acidified (only the 125 mL FLPE bottles), because several analytical methods (ICP-QMS, ICP-AES) were used, and measured in batches of about 100 samples. Otherwise, it would not have been possible to repeat measurements at a later time. The conditioning of 2000 new FEP could not be done, however, within the time and funding available. The surface of FEP bottles can be contaminated during production, and would first have to be treated with concentrated ultrapure HNO_3. The FLPE bottles from the firm Nalgene USA, which were used for the ICP-QMS and ICP-AES analyses, have an inner Teflon lining, thus needing no conditioning. The Sarstedt test tubes used for the automated sampler were checked using blanks, and no measurable contamination was observed.

Calibration standards containing all of the 61 elements measured by ICP-QMS are not readily available for purchase. Consequently, a calibration standard solution was prepared from the Merck CertiPUR ICP Multielement Standard Solution VI (containing 30 elements at 10–100 mg/L), the Merck CertPUR single element standards (1000 mg/L each of all the minor elements and REE), and the Merck CertiPUR standard solution containing 10,000 mg/L each of the major elements (Na, Mg, Al, K, Ca, and Fe). This calibration standard solution (W 1) was acidified with ultrapure HNO^3, and for the calibration measurements was subsequently diluted to the approximate concentrations in the bottled water samples. A second multielement calibration standard solution was prepared from the Merck CertiPUR single element standards (with concentrations of 1000 mg/L each for Ti, V, Cr, Ge, As, Se, Zr, Nb, Mo, Sn, Sb, Te, Hf, Ta, W, Hg and Pb), and the Merck CertiPUR standard solution containing 10,000 mg/L each of the major elements (Na, Mg, Al, K, Ca, and Fe). This calibration standard solution (W 2) was acidified with HCl (7 mL), and for the calibration measurements was subsequently diluted to the approximate concentrations of the elements

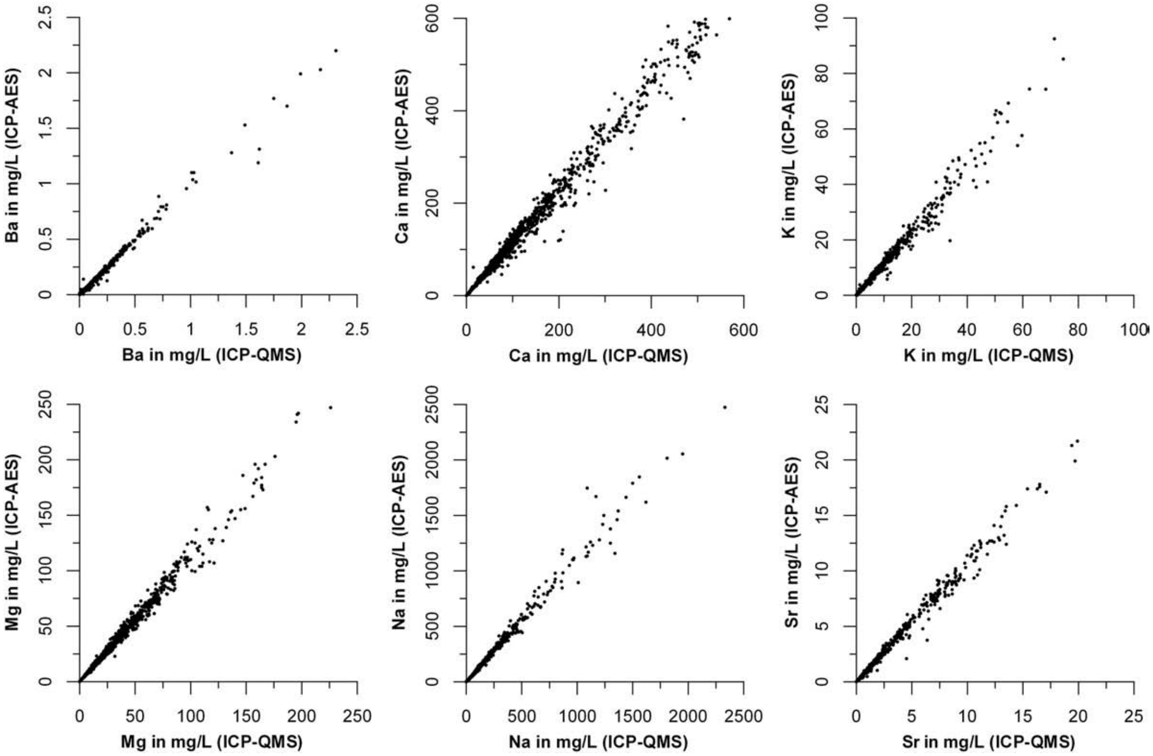

Fig. 1. Comparison of the analytical results of the ICP-QMS and ICP-AES methods in all European bottled water.

Table 7
Statistical parameters of elements determined on the blank solutions (in μg/L, n = 12).

Element	Mean	Standard deviation (SD)	3*SD	10*SD	Element	Mean	Standard deviation (SD)	3*SD	10*SD
Ag	0.0002	0.0001	0.0004	0.0013	Mo	0.005	0.003	0.009	0.029
Al	0.09	0.05	0.15	0.52	Nb	0.0014	0.0004	0.0013	0.0044
As	0.005	0.003	0.009	0.029	Nd	0.00040	0.00014	0.00042	0.00141
B	0.72	0.23	0.68	2.27	Ni	0.002	0.001	0.004	0.012
Ba	0.004	0.002	0.005	0.018	Pb	0.0026	0.0005	0.0016	0.0054
Be	0.0006	0.0003	0.0008	0.0027	Pr	0.00005	0.00004	0.00011	0.00037
Bi	0.0009	0.0003	0.0010	0.0034	Rb	0.0017	0.0007	0.0020	0.0068
Cd	0.0007	0.0002	0.0006	0.0021	Sb	0.0018	0.0007	0.0021	0.0068
Ce	0.00008	0.00005	0.00016	0.00053	Sc	0.004	0.003	0.0089	0.0296
Co	0.0019	0.0015	0.0046	0.0154	Se	0.006	0.002	0.006	0.021
Cr	0.046	0.009	0.028	0.094	Sm	0.00028	0.00014	0.00043	0.00143
Cs	0.0006	0.0003	0.0008	0.0026	Sn	0.0051	0.0015	0.0045	0.0150
Cu	0.007	0.005	0.014	0.048	Ta	0.0008	0.0003	0.0009	0.0030
Dy	0.00024	0.00009	0.00028	0.00092	Tb	0.00006	0.00002	0.00007	0.00024
Er	0.00019	0.00005	0.00015	0.00048	Te	0.005	0.003	0.0075	0.0251
Eu	0.00009	0.00003	0.00010	0.00033	Th	0.00017	0.00011	0.00034	0.00112
Fe	0.01	0.00	0.01	0.04	Ti	0.0023	0.0080	0.0241	0.0805
Ga	0.0003	0.0008	0.0024	0.0080	Tl	0.0014	0.0002	0.0005	0.0017
Gd	0.00027	0.00013	0.00038	0.00125	Tm	0.00004	0.00002	0.00006	0.00021
Ge	0.002	0.001	0.0033	0.0112	U	0.00016	0.00010	0.00031	0.00102
Hf	0.0002	0.0001	0.0002	0.0008	V	0.063	0.010	0.029	0.098
Ho	0.00075	0.00012	0.00036	0.00121	W	0.046	0.004	0.011	0.036
I	0.03	0.02	0.05	0.16	Y	0.00003	0.00004	0.00013	0.00042
La	0.00008	0.00003	0.00010	0.00034	Yb	0.00016	0.00009	0.00027	0.00088
Li	0.02	0.01	0.03	0.10	Zn	0.02	0.01	0.032	0.105
Lu	0.00004	0.00002	0.00005	0.00017	Zr	0.0003	0.0002	0.0007	0.0023
Mn	0.006	0.004	0.013	0.044					

in the bottled water samples. For the ICP-QMS analyses, 1:100 of the two multielement standard solutions were prepared daily.

The calibration standards for the ICP-QMS analyses were prepared in FEP bottles which were first cleaned with 65% HNO_3 (Merck Suprapur, density 1.41 kg/L) in a quartz apparatus (Kürner, Rosenheim, Germany), followed by rinsing with deionized water.

The standards were prepared using 1000 μL and 5000 μL Eppendorf pipette tips to pipette concentrated solution into the PEP bottles, brought to the required concentration with deionized water from a FEP bottle by weighing and then acidified with 69% HNO_3 (Roth Ultrapure, density 1.41 kg/L) to 1% weight using Brand Handystep electronic repeating pipettes and Eppendorf Combitips.

5. Quality control

The river water reference material SLRS-4 from the National Research Council Canada, and the low-level fortified standards for trace elements TM-26.3, TM-27.2, TM-28.2 and TM-28.3 from the National Water Research Institute of Canada were used for quality control purposes. All certified reference samples were obtained in 500 mL HDPE bottles. In addition, an internal laboratory mineral water standard (MinWas) was used (Tables 4–6). This sample was repeatedly measured for the entire period the bottled water samples were analyzed to monitor the reproducibility of the measurements. The internal laboratory standard was stored in a 5 L HDPE canister. Standard SLRS-4 was measured 103 times at regular intervals during sample analyses. Results are presented in Table 4, and demonstrate that for most elements the determined results are well in agreement with the certified values.

When analyzing as many elements as in this study, a general problem is that there are no suitable reference materials that are certified for all these elements. However, published values for SLRS-4 from other investigations are provided in Table 4. Nearly all measured values are very close to the certified and/or published results. The low-level fortified standards for trace elements TM-26.3, TM-27.2, TM-28.2 and TM-28.3 were measured from 25 to 91 times, evenly spread over the whole period of analysis of the bottled water samples (Tables 4 and 5). These standards cover different concentration ranges for a number of elements and, thus, show that many elements that are problematic at low concentrations deliver reliable results at higher values. The coefficient of variation was used for general quality evaluation (Tables 4 and 5). The certified values, and the produced results, are well in agreement for most elements. The international and internal (MinWas) standards were only measured by ICP-QMS over the entire period of the project (Tables 4 and 5).

The MinWas laboratory standard was measured 261 times to assess the precision of the measurements at the concentrations of this standard. Comparison of the coefficient of variation, obtained for the two frequently analyzed standards (SLRS-4 and MinWas), shows that for a number of elements with low concentrations (e. g. Ag, Ga, Hf, Nb, Sn, Ta, Te, Tl, and W) the coefficient of variation is high (CV>25%). Measured values for each element in the standards were plotted, showing that only for a few elements (Hf, Nb, Sn, Ta and W) there appears to be an overall problem with reproducibility at very low concentrations near the instrument detection limit of these elements in the standards. Consequently, results for these few elements need to be treated with care in the concentration range up to 10 times the instrument detection limit. The results for other standards demonstrate, however, that the determined values are reliable at higher concentrations.

The element Sc was measured, but is not reported here due to an interference with Si, causing too high values. This problem can only be overcome by the use of a high resolution ICP-MS.

Several of the major elements (Ca, K, Mg, and Na) can reach such high concentrations in water samples that they are above the upper determination limit of the ICP-QMS method and the samples would need to be diluted for reliable measurement. To ensure the reliability of results, these elements were also measured by ICP-AES and the ICP-AES results are reported in EGS (2010). The analytical results from the two methods (ICP-AES vs. ICP-QMS) are compared for a number of elements in Fig. 1. The ICP-QMS results for major elements were only used for comparison (as an additional quality check).

The accuracy of the results was confirmed in ring experiments. All of the BGR laboratories participating in this survey (especially the ones doing the ICP-AES analyses) have participated in several ring experiments per year involving water analyses (r-concept E0711, water standard, lake water, waste water; r-concept E0810, water standard, surface water, waste water; r-concept N/P0741, water standard, waste water; r-concept 0911, water standard, surface water, waste water; r-concept E1009, water standard, surface water, waste water), as well as the analysis of solids (GeoPT 21–26; Wageningen ISE 2008-1, 2008-2, 2008-3, 2008-4; Wageningen ISE 2009-1, 2009-2, 2009-3, 2009-4; r-concept E0711, soil, sewage sludge).

In addition, duplicates were analyzed at regular intervals and a number of quintuple and ten-fold determinations were also carried out. The results are quite comparable to those for the standards presented above. In total, 128 duplicate pairs were used to calculate the overall precision of the analytical results at the 95% confidence level, and to estimate the practical detection limits (PDL, Table 1); however, care with the interpretation of these values is needed in the case of water samples due to the very wide concentration range observed for many elements (Thompson and Howarth, 1978; Reimann and Wurzer, 1986). A reliable estimate of the PDL depends essentially on the concentration range of the element in the duplicates in relation to the IDL. If there are not sufficient duplicate pairs near the IDL a too high value of the PDL may result. For the calculation of the overall precision the concentration range into which the duplicates fall in relation to the overall variation is important. Nevertheless, these parameters provide a further impression of the overall quality of the analyses performed in this project, and they are thus given in Table 1.

Sample blanks were measured over the entire time span of the project. The blanks were prepared in a 500 mL FEP bottle by adding 400 g of deionized water (SERALPUR-90; 18.2 MΩ), and 4 mL 69% HNO_3 (Roth Ultrapure, density 1.41 kg/L). A 50 mL Sarstedt test tube was filled with solution and then measured 10 or 12 times.

The IDL (instrument detection limit) and the RDL (reported detection limit) were estimated from the blank measurements. The instrument detection limit (Table 1) was determined as three times the standard deviation of the sample blank (Table 7). The reported detection limit (RDL) was calculated as ten times the standard deviation of the sample blank. Thus, the RDL is always larger than the IDL. The Wisconsin Department of Natural Resources (1996) calls the RDL also as "Limit of Quantitation" (LOQ). The instrument detection limit (IDL), calculated from measurement runs by the ICP-QMS system was used for some elements (B, Bi, Co, Cr, Dy, Ga, Gd, Hf, Ho, I, Li, Mn, Mo, Nd, Pr, Rb, Sb, Sc, Sm, Sn, Ta, Te, Th, Ti, U, V, Y, Yb, Zn, and Zr). The IDL is considered the minimum detection concentration for the instrument only (Jones and Clarke, 2005).

It is finally noted that a number of elements in the standards are not included in the certified values. These elements were used for quality control purposes, when the coefficient of variation and the blanks indicated that they are reliable.

6. Overview and conclusions

Since the beginning of 2010, there were a total of 1916 mineral water brands officially registered in Europe. For this study, 1785 bottled water samples were purchased from European supermarkets and analyzed for more than 70 parameters in the laboratories of the BGR in Hannover.

A combination of the following techniques was used to analyze the bottled water samples of this study: quadrupole inductively coupled emission spectroscopy (ICP-QMS, trace elements), inductively coupled plasma atomic emission spectroscopy (ICP-AES, major elements and PO_4^{3-}), ion chromatography (IC, anions), atomic fluorescence spectrometry (AFS, Hg), titration (alkalinity), photometric methods (NH_4^+), potentiometric methods (pH), and conductometric methods (electrical conductivity, EC, Table 1).

Sample preparation and ICP-QMS analyses were carried out in a clean room (clean room class 10,000). Details of instrument settings and scanning conditions are given in Table 2.

A number of elements still pose special problems during ICP-QMS analyses, such as (a) Sc detection is seriously disturbed by Si), (b) interference corrections must be made for the numerous overlaps of the various REE oxide peaks. Many of the REEs require 3–4 such corrections in order to obtain accurate results, and (c) I is another notorious element for determination by ICP-QMS. The measured iodine concentrations were, however, reproducible over the entire period of the project. The mass spectrometer measurements were made on ^{127}I.

Quality control was very thorough and consisted of the:

(1) measurement of a number of international reference materials to document the accuracy of the analytical results,

(2) frequent measurement of an internal project standard (MinWas) to check the accuracy of the results for the determined parameters,

(3) frequent measurement of sample blanks to detect any contamination and to derive reliable detection limits,

(4) frequent analysis of 128 sample duplicates to estimate the analytical precision of measurements, and

(5) participation of the analytical laboratory in several ring experiments, which are carried out routinely every year.

In total, 23 elements were also determined by ICP-AES. These were used for an additional internal quality control of the ICP-QMS values. A general problem when analyzing such a large number of elements, as in this particular study, is that there no suitable reference materials (standards), which are certified for all these elements.

Furthermore, the analytical results given on the bottle labels were compared with those obtained in the BGR laboratories, and most bottled water samples with higher than usual concentrations were reanalyzed in order to be absolutely certain that no mistakes were made during analysis.

In conclusion, the high quality dataset for bottled water in the European Groundwater Geochemistry atlas (EGS, 2010) provides a first impression of the natural concentrations and variations of the determined chemical elements and additional parameters in groundwater at the European scale.

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