Application of ICP Sector Field MS and Principal Component Analysis for Studying Interdependences among 23 Trace Elements in Polish Beers

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Twenty-three metallic elements, including almost all essential and toxic metals such as lead, cadmium, mercury, arsenic, silver, and thallium, have been quantified in 35 types of bottled and canned Polish beer by using double-focusing sector field inductively coupled plasma mass spectrometry (ICP−MS) with ultrasonic nebulization. The samples were digested using concentrated HNO_3 in closed PTFE vessels and applying microwave energy under pressure. The means and medians of the concentrations of Rb, Mn, and Fe were on the order of 200 ng/mL; Cu, Zn, V, Cr, Sn, As, Pb, and Ni were detected at 1−5 ng/mL; Ag, Ga, Cd, Co, Cs, Hg, U, and Sb were found at < 1 ng/mL; and In, Tl, Bi, and Th were present at < 0.1 ng/mL. The concentrations of Hg, Cd, As, Pb, and Zn were 1−3 orders of magnitude lower than proposed tolerance limits. The interdependences among determined trace elements were examined using the principal component analysis (PCA) method. The PCA model explained 74% of the total variance. The metals tend to cluster together (As, Tl, Cs, Sn, Th, Bi, and Hg; Cd and Co; Cs and Cr; Fe and Zn; Mn and V).

Keywords: *Metallic elements; toxic elements; trace elements; beer; principal component analysis*

INTRODUCTION

Beer has been defined as a beverage obtained from alcoholic fermentation of malted cereal, usually barley malt, with or without starchy materials and to which hops have been added (*1*). Hoyrup's *Encyclopedia of Chemical Technology* defined lager beer as a brew from barley malt, which is stored for a period of time for clarification and maturing (*2*). Beer is also considered the generic term for all malt beverages called beer, ale, stout, porter, and lager (*1*).

In Poland, barley malt has the unique position as the preferred, and practically the only, cereal used for brewing beer. Beer drinking has been steadily increasing in recent decades even in countries where alcoholic beverages are not traditional (*3*). A review of the scientific literature on the positive benefits of light and moderate alcohol consumption suggests that beer contains small percentages of recommended daily allowances of vitamins and significant proportions of recommended daily allowances of trace metals and minerals (*4*). Beer consumption already makes up a sizable percentage of total alcohol consumption in Poland, and consumers expect a natural high-quality drink.

The metallic elements characterization of beer has a lot of interest because their concentrations can influence its quality, including organoleptic characteristics and stability, as well as the health status of the consumers (*5*−*7*). It was therefore of interest to ascertain the quality of various Polish beers through knowledge of the concentrations of many metallic elements. It was also of interest to include those elements commonly considered toxic, and to determine as well how their concentrations comply with present legislation in Poland. Furthermore, the objectives were to assess and explain possible origins of, and interdependences among, trace element concentrations in Polish beers using the principal component analysis (PCA) method.

MATERIALS AND METHODS

Materials. Thirty-five brands of beer (30 bottled, 5 canned), all manufactured and commercially available in Poland, were analyzed with respect to 23 elements (Ga, In, Sn, Hg, Tl, Bi, As, Sb, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Rb, Cs, Pb, Th, and U). The samples were randomly collected from local stores in 1996 and represent the types of beers readily available to consumers. The beer brands originated from the nine leading beer manufacturers in Poland: Bielkówko, Elbląg, Gdańsk, Leżajsk, Poznań, Okocim, Szczecin, Tychy, and Żywiec brewer-

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Table 1. Beer Samples Data Sheet

beer	brewery	type of beer	type of container[a]	alcohol content (% by vol)	extract content (% by wt)	code no.
Amber Red	Bielkówko	full light	B	6.3	14.3	1
Koźlak	Koźlak	dark strong	B	7.5	18	2
EB Specjal	Elbrewery	full light	B	5.4	11.5	3
Specjal	Elbrewery	full light	B	5.6	12.5	4
Porter	Elbrewery	porter	B	9.2	22.0	5
Red Original	Elbrewery	red	B	5.9	13.0	6
Tyskie Książęce	Tyski	full light	B	5.4	12.0	7
Hevelius	Hevelius	full light	B	5.9	13.5	8
Artus	Hevelius	full light	B	5.8	12.5	9
Gdańskie	Hevelius	full light	B	5.6	12.5	10
Kaper Królewski	Hevelius	porter	B	7.8	20.0	11
Karmela	Hevelius	nonalcoholic	B	1.2	8.0	12
Lech Premium	Lech	full light	B	5.3	10.3	13
Lech Premium Lager	Lech	full light	B	5.4	11.3	14
Dziesięć i pół	Lech	full light	C	5.3	10.5	15
Okocim	Okocim	full light	B	4.9	10.5	16
Okocim Zagłoba	Okocim	full light	B	5.4	11.5	17
Okocim Mocne	Okocim	porter	B	7.5	15.1	18
Karmi	Okocim	nonalcoholic	B	1.2	10.4	19
Okocim Export Specjal	Okocim	full light	C	5.7	12.5	20
Okocim Light Beer	Okocim	full light	C	4.9	10.5	21
Dziesięć i pół	Poznań	full light	B	5.3	10.5	22
Kapitan Beer	Szczecin	full light	B	6.3	14.0	23
Bosman Beer Pils	Szczecin	full light	B	5.3	11.0	24
Bosman Beer	Szczecin	full light	B	6.5	12.5	25
Bosman Beer Specjal	Szczecin	full light	B	6.3	14.0	26
Kosher Szaron Beer	Szczecin	full light	B	5.6	12.5	27
Krzepkie	Szczecin	strong	B	8.1	20.0	28
Warka Strong	Warka	strong full light	B	7.3	15.0	29
Leżajsk	Leżajsk	full light	B	5.0	11.0	30
Żywiec	Żywiec	full light	B	5.6	12.5	31
Leżajsk	Leżajsk	full light	C	5.0	11.0	32
Żywiec Krakus	Żywiec	full light	B	5.4	11.7	33
Żywiec Porter	Żywiec	dark strong	B	9.2	22.0	34
Żywiec Beer	Żywiec	full light	C	5.6	12.5	35

[a] B, bottle; C, can.

ies (Table 1). All examined samples of beer, on the basis of their alcohol and extract content, could be categorized into light beers such as full light, strong full light, red, and nonalcoholic, and dark beers such as strong, dark strong, and porter.

Analytical Methods. Samples (1 mL of degassed beer) were digested in closed vessels made of poly(tetrafluoroethylene) (PTFE) in an automatic microwave digestion system (MLS 1200) using concentrated nitric acid (5 mL). The microwave parameters were 300 W of power for 30 min, held with no power for 30 min, and then 600 W of power for 60 min. All reagents used were of the analytical grade (Kanto Chemical Co, Inc., Elgrade 1.38, Japan). After the vessels were cooled at room temperature, they were opened to check whether the complete dissolution had occurred. The product was transferred to a 50-mL volumetric flask and diluted with ultrapure Milli-Q water.

Measurements were carried out using a double-focusing sector field inductively coupled plasma−mass spectrometer Plasma Trace (VG Elemental, UK) equipped with an ultrasonic nebulizer USN (Applied Research Laboratories, Switzerland) (Table 2). The digested sample was diluted 10-fold by using double-distilled water, and Rh was added as an internal standard at 200 ng/mL. An external calibration was performed by running a blank (ultrapure water acidified with ultrapure HNO_3) and multi-element standard solutions with concentrations of 1, 10, and 100 ng/mL. The sample preparation and measurements were performed under ultra-clean conditions in a clean room class 100 or clean booth class 1000 to prevent sample contamination from laboratory air. All containers were placed in 1% purified nitric acid for over a month and thoroughly rinsed with double-distilled water prior to use. The analytical method used was intensively validated using, among others, standard reference materials such us SRW 1643c (trace elements in water) provided by the National Institute of Standards and Technology, and SLRS-2 (riverine water) supplied by the National Research Council of Canada (*8*).

Table 2. Analytical Conditions for ICP−MS

parameter	condition
generator	
maximum power	1.2 kW
frequency	27.12 MHz
argon gas flow rate	
coolant	14.0 L/min
plasma	0.7 L/min
carrier	1.0 L/min
sample flow rate	1.8 mL/min
ultrasonic nebulizer (USN)	
heated tube temp.	120 °C
cooling bath temp.	1 °C

m/z and abundance for each element

element	*m/z*	abund.	element	*m/z*	abund.	element	*m/z*	abund.
V	51	99.8	Ga	69	60.1	Hg	202	29.8
Cr	52	83.8	As	75	100	Tl	205	70.5
Mn	55	100	Rb	85	72.2	Pb	208	52.4
Fe	56	91.7	Ag	107	51.8	Bi	209	100
Co	59	100	Cd	111	12.8	Th	232	100
Ni	58	68.3	Sn	120	32.6	U	238	99.3
Cu	65	30.8	Sb	121	57.3			
Zn	66	27.9	Cs	133	100			

In day-by-day laboratory runs, with every set of 10 real beer samples one blank sample was digested, diluted, and anlyzed. For blank samples no major interferences were found for the elements quantified. Discrepancies between certified values and concentrations quantified were below 5%.

Data Analysis. All statistical analyses were performed with computer software Statistica version 5.0. Principal component analysis, also known as principal factor analysis mathemati-

Table 3. Trace Metals (ng/mL) in Polish Beers

beer	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As	Cd	In	Tl	Pb	Bi	Co	Rb	Cs	Hg	Th	U	Sn	Sb	Ag
Amber Red	48	4.6	160	76	6.2	64	40	0.05	8.1	0.19	0.005	0.064	1.8	0.032	0.10	190	0.21	0.64	0.094	0.48	1.1	0.54	0.08
Koźlak	17	8.4	360	78	12	79	27	0.09	10	0.06	0.004	0.100	2.9	0.025	0.12	330	0.83	0.36	0.059	0.19	1.4	0.44	0.02.
EB Specjal	47	3.8	160	120	5.3	44	14	0.07	13	0.09	0.004	0.032	1.4	0.014	0.11	150	0.14	0.36	0.058	0.33	0.77	0.57	0.02
Specjal	13	15	150	140	5.3	56	16	0.09	6.6	0.03	0.007	0.027	2.3	0.060	0.12	180	0.16	0.26	0.069	0.28	1.8	0.42	0.05
Porter	27	26	470	310	200	54	11	0.15	9.5	0.11	0.006	0.055	3.8	0.038	0.56	370	0.39	0.35	0.120	0.31	3.0	0.57	0.01
Red Original	21	4.4	240	160	8.6	86	12	0.06	12	0.12	0.015	0.051	3.0	0.024	0.35	270	0.27	0.44	0.093	0.15	3.0	0.32	0.02
Tyskie Książęce	23	25	160	430	18	64	34	0.06	8.2	0.35	0.007	0.037	3.7	0.13	0.50	210	0.19	0.28	0.059	0.10	1.4	0.34	0.07
Hevelius	18	12	190	340	8.7	82	25	0.07	7.7	0.50	0.017	0.065	6.0	0.12	0.40	150	0.27	0.16	0.100	0.38	2.7	0.43	0.20
Artus	13	38	180	270	25	38	8.0	0.04	3.6	0.20	0.004	0.059	3.0	0.063	0.48	220	0.24	0.27	0.096	0.19	1.2	0.24	0.05
Gdańskie	24	45	110	180	9.9	31	12	0.05	9.3	0.22	0.008	0.053	3.5	0.091	0.25	130	0.19	0.08	0.045	0.12	1.6	0.40	0.03
Kaper Królewski	25	9.9	150	130	7.5	54	19	0.03	7.9	0.53	0.004	0.085	3.4	0.023	0.26	380	0.40	0.29	0.260	0.61	1.3	0.91	0.01
Karmela	22	9.9	120	240	6.3	59	17	0.06	8.9	0.09	0.011	0.055	1.9	0.046	0.23	150	0.28	0.25	0.071	0.17	3.0	0.38	0.03
Lech Premium	27	14	230	180	9.1	78	14	0.13	9.6	0.22	0.007	0.028	4.3	0.481	0.52	130	0.16	0.25	0.051	0.29	2.0	0.58	0.03
Lech Premium Lager	17	11	210	130	3.9	60	17	0.03	4.2	0.10	0.006	0.023	3.4	0.027	0.29	130	0.17	0.27	0.045	0.20	1.2	0.32	0.03
Dziesięć i pół	30	11	260	130	4.5	71	7.0	0.03	6.4	0.12	0.006	0.025	2.7	0.021	0.13	120	0.12	0.12	0.068	0.33	0.83	0.46	0.02
Okocim	13	13	65	390	7.8	36	19	0.07	5.8	0.03	0.001	0.018	2.5	0.025	0.30	130	0.19	0.44	0.058	0.04	1.1	0.25	0.02
Okocim Zagłoba	15	10	100	120	10	110	37	0.02	2.2	0.06	0.006	0.025	3.2	0.230	0.32	240	0.20	0.53	0.032	0.06	1.6	0.22	0.04
Okocim Mocne	9.0	15	170	150	6.5	32	20	0.09	4.2	0.02	0.005	0.087	2.4	0.057	0.11	270	0.23	0.23	0.036	0.07	1.0	0.26	0.05
Karmi	19	22	120	490	6.2	48	39	0.21	4.0	0.25	0.003	0.099	2.2	0.013	0.30	91	0.17	0.33	0.094	0.09	1.1	0.32	0.02
Okocim Export	11	9.0	90	70	5.6	35	10	0.15	3.3	0.16	0.007	0.030	2.3	0.019	0.11	220	0.22	0.42	0.024	0.08	0.65	0.20	0.02
Okocim Light Beer	12	23	130	140	9.2	38	7.0	0.11	2.3	0.04	0.005	0.025	2.2	0.095	0.41	180	0.15	0.19	0.029	0.06	0.66	0.22	0.11
Dziesięć i pół	17	7.6	230	86	3.8	70	22	0.05	5.4	0.12	0.010	0.030	2.5	0.017	0.16	110	0.15	0.27	0.025	0.05	2.1	0.29	0.05
Kapitan Beer	17	26	240	120	10	57	28	0.04	3.8	0.06	0.004	0.046	2.0	0.065	0.25	110	0.30	0.22	0.080	0.42	1.3	0.39	0.06
Bosman Beer Pils	18	25	190	150	11	62	47	0.06	3.9	0.07	0.009	0.044	2.6	0.044	0.26	88	0.26	0.40	0.076	0.38	1.2	0.41	0.07
Bosman Beer	16	7.7	150	86	8.9	68	14	0.01	2.8	0.04	0.007	0.036	3.8	0.016	0.19	230	0.33	0.55	0.066	0.36	0.91	0.22	0.02
Bosman Specjal	23	4.3	220	65	8.4	69	14	0.05	4.0	0.05	0.005	0.046	2.1	0.007	0.17	130	0.27	0.35	0.071	0.45	0.62	0.29	0.03
Kosher Szaron	15	3.8	200	71	8.9	86	31	0.05	2.5	0.04	0.003	0.036	2.5	0.007	0.15	160	0.26	0.25	0.030	0.19	0.52	0.17	0.02
Krzepkie	36	4.4	270	83	13	147	14	0.01	4.8	0.08	0.001	0.057	3.5	0.013	0.15	200	0.35	0.21	0.084	0.69	0.77	0.67	0.01
Warka Strong	28	8.5	100	100	5.4	29	4.0	0.05	5.5	0.16	0.006	0.033	1.8	0.009	0.13	410	0.44	0.60	0.051	0.58	0.85	0.55	0.02
Leżajsk	8.0	20	120	45	4.1	49	8.0	0.01	3.6	0.07	0.008	0.032	2.4	0.007	0.08	210	0.20	0.17	0.024	0.08	0.79	0.16	0.03
Żywiec	32	4.0	97	140	6.3	110	9.0	0.01	5.2	0.07	0.005	0.028	1.9	0.009	0.09	190	0.16	0.21	0.041	0.39	0.54	0.55	0.03
Leżajsk	25	11	110	100	5.7	67	13	0.05	5.7	0.06	0.001	0.047	2.0	0.005	0.12	150	0.19	0.15	0.036	0.18	0.42	0.17	0.02
Żywiec Krakus	20	4.4	62	110	4.3	53	11	0.03	8.0	0.06	0.006	0.016	1.4	0.007	0.10	210	0.18	0.09	0.031	0.17	0.68	0.42	0.02
Żywiec Porter	55	17	350	530	8.7	58	120	0.03	11	0.40	0.015	0.150	6.0	0.010	0.57	330	0.50	0.38	0.046	0.20	3.4	0.46	0.03
Żywiec Beer	27	6.1	53	210	5.8	86	32	0.02	3.8	0.07	0.007	0.033	2.0	0.007	0.09	200	0.23	0.37	0.052	0.42	0.49	0.42	0.03
median	20	11	160	130	7.8	60	16	0.05	5.5	0.09	0.006	0.037	2.5	0.024	0.19	190	0.22	0.27	0.058	0.20	1.1	0.39	0.03
mean	23	14	180	180	14	64	22	0.06	6.2	0.14	0.006	0.048	2.8	0.053	0.24	200	0.26	0.31	0.065	0.26	1.3	0.39	0.04
maximum	55	45	470	530	200	150	120	0.21	13	0.53	0.017	0.150	6.0	0.480	0.57	410	0.83	0.64	0.262	0.69	3.4	0.91	0.20
minimum	8.0	3.8	53	45	3.8	29	4.0	0.01	2.2	0.02	0.001	0.016	1.4	0.005	0.08	88	0.12	0.08	0.024	0.04	0.42	0.16	0.01
proposed limit	-	-	-	-	-	-	2000	-	100	20	-	-	100	-	-	-	-	10	-	-	-	-	-

Table 4. Factor Loadings Obtained with Unrotated Factor Matrix[a]

eigenvalues	9.375461	2.458627	1.990398	1.703264	1.467246
total variance (%)	40.76287	10.68968	8.653906	7.405496	6.379332
	Factors				
variables	PC1	PC2	PC3	PC4	PC5
V	−0.08463	−0.66057	0.202872	0.078305	0.127499
Cr	0.808991	−0.01083	−0.09348	−0.02096	−0.38907
Mn	−0.27374	−0.52555	0.038617	0.101877	0.323588
Fe	−0.14998	−0.61617	−0.26796	−0.40484	−0.39468
Ni	0.82277	0.398964	0.156099	−0.00944	0.145451
Cu	0.192284	−0.25272	−0.23916	0.418633	0.690373
Zn	0.141952	−0.80614	−0.04269	−0.35181	−0.08343
Ga	0.43273	−0.23658	−0.26834	0.538825	−0.01556
As	0.903362	−0.08995	0.177275	−0.17949	0.113067
Cd	0.64098	−0.25398	−0.06476	0.181238	−0.09638
In	0.248733	0.003445	−0.2906	−0.64797	0.459267
Tl	0.826704	−0.08705	0.2321	−0.31565	0.092393
Pb	0.54887	0.172074	−0.64953	−0.17404	−0.0565
Bi	0.948601	0.004941	0.105444	−0.02746	−0.01298
Co	0.697599	−0.28773	−0.3479	0.200606	0.054551
Rb	−0.10004	−0.29521	0.674494	0.31578	−0.19492
Cs	0.751128	−0.1426	0.2993	−0.1992	0.105123
Hg	0.871326	−0.10844	0.190582	0.025534	−0.08853
Th	0.872082	−0.10938	0.154587	0.125946	0.174588
U	0.776772	0.172322	−0.03965	0.128192	−0.13502
Sn	0.797878	0.097722	0.241008	−0.00327	−0.23307
Sb	0.749399	0.236187	−0.0613	0.021395	0.171971
Ag	0.373603	−0.13624	−0.56186	0.322959	−0.31112

[a] Minimum eigenvalue =1, number of factors = 5, log(10) determinant of correlation matrix = −11.59.

cally, is the matrix decomposition into means x_k^{mean}, scores t_{ia}, loading p_{ak}, and residuals e_{ik} according to the following equation:

$$x_{ik} = x_k^{mean} + \sum_{a=1}^{A} t_{ia} p_{ak} + e_{ik}$$

where x_{ik} are the descriptors compiled in the multivariate characterization. The index i is used for the compounds (i = 1,2,3...35), and index k is used for the descriptors (k = 1,2,3...23). Each score t_{ia} describes the location of the i-th compound along a-th principal component (PC) at the score plot. The absolute value of a loading p_{ak} informs how much the descriptor (variable k) contributes to the a-th PC. The sign of a loading shows if the variable is positively or negatively correlated to the PC. The first calculated principal component explains the main variation in the data, the second represents the next largest variance, and so on (*9*−*11*).

The extraction of principal components amounts to a variance maximizing (varimax) rotation of the original variable space. This type of rotation is called variance maximizing because the criterion for (goal of) the rotation is to maximize the variance (variability) of the "new" variable (factor), while minimizing the variance around the new variable.

The rotational orientation of axes in factor analysis is more or less arbitrary. However, numerous rotational strategies have been proposed to choose an orientation of axes that is most interpretable (i.e., approximates a simple structure). There are various rotational strategies that have been proposed. The goal of all of these strategies is to obtain a clear pattern of loadings, that is, factors that are somehow clearly marked by high loadings for some variables and low loadings for others. Typical rotational strategies are varimax, biquartimax, quartimax, and equamax. However, the oblique factors produced by such rotations are often not easily interpreted.

The method that is most commonly used and referred to as *varimax rotation* is aimed at maximizing the variances of normalized factor loadings across variables for each factor; this is equivalent to maximizing the variances in the columns of the matrix of normalized factor loadings. The method that is commonly referred to as *quartimax rotation* is aimed at maximizing the variances of normalized factor loadings across factors for each variable; this is equivalent to maximizing the variances in the rows of the matrix of normalized factor loadings (*9*−*11*).

RESULTS AND DISCUSSION

The data on concentrations of metallic elements quantified in Polish beers indicated negligible levels of toxic metals such as mercury, arsenic, cadmium, lead, thallium, and silver (Table 3). The proposal regarding an update of the legislative act on the "hygienic conditions of food" existing in Poland sets the tolerance concentration for selected metallic elements in beer as 10 (Hg), 20 (Cd), 100 (As, Pb), and 2000 (Zn) ng/mL (*12*). The quantified concentrations of mercury (0.08−0.64 ng/mL), cadmium (0.02−0.53 ng/mL), arsenic (2.2−13 ng/mL), lead (1.4−6.0 ng/mL), and zinc (4.0−120 ng/mL) in randomly collected beer samples are much smaller than these proposed tolerance limits.

In this study, some differences of the element concentrations in beer were observed (Table 2), depending on the type of beer, but also among the particular beer type, and even for beer stocks that originated from the same brewery but were differently packaged. The concentrations of some metallic elements (cadmium, iron, zinc, chromium, copper, lead, and tin) noted in this study were substantially smaller than those previously reported for the Polish beers by other authors (*13*, *14*), and in any case did not exceed permissible element concentrations.

The high quality of the beer brands examined, with regard to their negligible concentrations of toxic elements, could be associated with the fact that beverages are prepared more carefully nowadays, using highest quality substrates, materials, and processing equipment. Furthermore, increasing demands of producers about the chemical composition of the materials and products used for beer brewing, including care in use of pesticides and fertilizers, could improve the situation toward the observed lower contamination level of the beverages. A study on aluminum content of nonalcohol

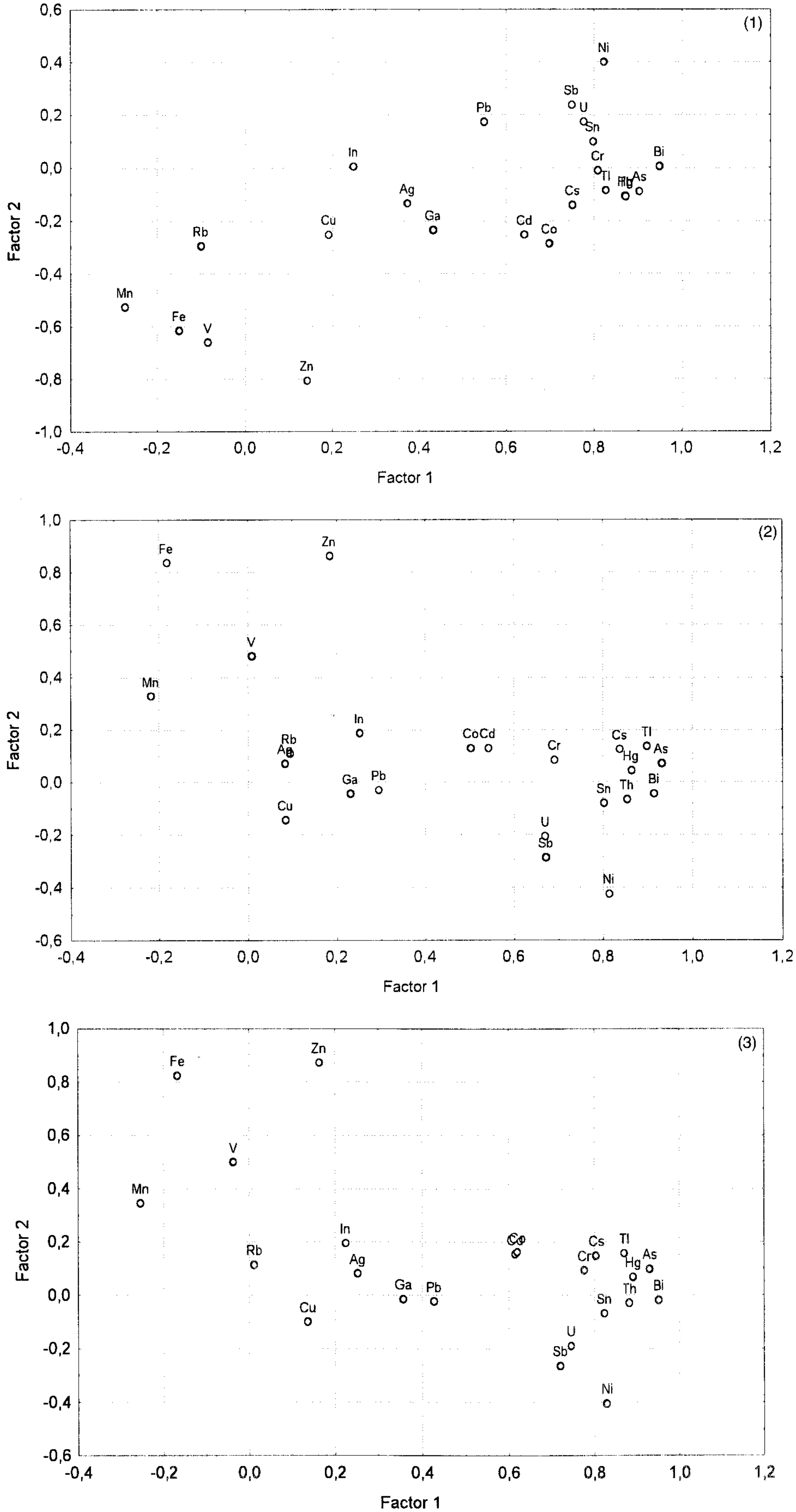

Figure 1. Principal component analysis of the trace metals ($n = 23$) in Polish beers. Associations among trace metals are shown on principal components 1 and 2 with unrotated (1), Varimax-rotated (2), and Quartimax-rotated (3) matrixes.

and alcoholic beverages (*5*) has indicated that this element may be leaching into beverages from their containers, thus affecting length of shelf life and concentration of the metallic elements, an interesting issue to investigate in the future.

The principal component analysis has been applied to analyze the correlation matrix obtained from a 23 × 35 data matrix. The correlation matrix shows that a certain degree of association exits between some elements. Absolute value of the correlation coefficient for some elements exceeds 0.90. The correlation matrix was computed for 23 variables by the principal component method and the results are shown in Table 4. The number of components was chosen with the Kaiser criterion – only factors with an eigenvalue greater than 1 have been retained (*9*, *15*).

The PCA of the data matrix projected a model that explained 74% of the total variance. The factor loading shows (Table 4) that the first PC (PC1) is strongly (absolute loadings value > 0.070) influenced by variables describing Cr, Ni, As, Tl, Bi, Cs, Hg, Th, U, Sn, and Sb. The second PC (PC2) is strongly influenced by negatively correlated Zn. The factor matrix obtained after the varimax and quartimax rotations corresponded with the data from the unrotated matrix and furthermore indicated stronger correlations between the principal component and the elements.

The comparison of the varimax-rotated factor matrix with the matrix obtained after a quartimax rotation shows no substantial difference between them. The rotation-transformed matrixes (data not shown) demonstrate that Ni, As, Tl, Bi, Cs, Hg, Th, and Sn (in quartimax-rotated also Cr, Sb, and U) are associated with the PC1 matrix, Fe and Zn are associated with PC2, whereas In and negatively correlated Rb are associated with PC3, Ag is associated with PC4, and Cu is associated with PC5. The values of loadings < 0.070 could also be significantly correlated with appropriate PC. Figure 1 shows graphically the interdependences among the elements in the factor space as a PCA plot.

The trace metals in beers may originate from natural sources (soil, water, cereal, hops, and yeast), as well as environmental contamination, fertilizers, pesticides, industrial processing, and containers. As can be read from Figure 1, metals tend to cluster together, for example As, Tl, Bi, and Hg cluster together (associated with PC1), Cr clusters with Cs as well as Co and Cd (also correlated with PC1). This configuration of cluster intercorrelations could be explained by considering that concentrations of trace metals in beer mainly depend on several factors, including presence of metals in raw material (barley); environmental, production, and container contamination (e.g., enamels and pigments); or interferences in the brewing process. Each metal cluster could be associated with a different source – it is clearly evident that the Co–Cd is related to cobalt powder use in the industry in processing of hard metals to produce containers as well for the preparation of enamels and pigments. Both are rare in the earth's crust (*16*). The As–Hg–Tl–Bi–Sn–Th–Hg and U–Sb clusters (both correlated with PC1) could be associated with industrial and other anthropogenic sources. Some similarities in the distribution pattern of these metals in the beers examined suggest an anthropogenic origin, most probably through airborne particle deposition followed by subsequent accumulation on plant (barley) and soil surfaces. The Fe–Zn cluster is observed in association with PC2. Because of their low costs, Fe and Zn are widely used together for application of zinc coating onto steel and other ferrous substrates as corrosion protection (*17*). The Mn–V cluster may be associated with the last two decades of interest in layered manganese and vanadium oxides for their potential use as secondary cathode materials for advanced lithium batteries (*18*, *19*). Furthermore, field experiments with various parts of the mustard plant (*Sinapsis alba*) indicated that root accumulation of vanadium was inhibited by Mn, Ni, and Cu (*20*). Nickel is also considered an essential micronutrient to some higher plants (*21*), which suggests accumulation of Ni by plants and could be considered a reason for the separation of Ni in the space matrix for the beers examined. The situation observed for the In–Rb cluster associated with PC3 could indicate a coexistence of these metals in the environment on some certain low level; rubidium naturally occurs in the earth crust at a concentration of 0.01%, whereas indium can hardly form mineral compounds and is mainly found in other ores (*22*, *23*).

Principal component analysis seems to be a promising tool to determine interdependences among trace metals in foodstuffs, especially because it is a method of multivariate projection designed to extract systematic variations in the data matrix. It can deal with many factors simultaneously (*24*, *25*). This feature is of special importance in chemistry, because interpretations of most chemical data require multivariate approaches.

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