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Trace element analysis of korean car windshield using LA-ICP-MS

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LA-ICP-MS를 이용한 한국 자동차 유리의 미량원소 분석

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Abstract : The analyses of minor and trace elements in glass debris were performed using LA-ICP-MS in order to identify manufacturers using real commercial samples. At first, a calibration curve was made using standard glass samples of NIST 610, 612, 614 and 616. ^{29}Si was used as an internal standard, and the ratios of metal/Si for each metal were compared with their concentrations. Based on elements in each sample and standard materials, 24 metals were quantified and the LOD in analysis, according to the blank sample, was in the range of 0.11 mg/kg (Ti)-4.91 mg/kg (Ca). Eleven samples from two manufacturers were collected and five sub-samples were taken from each sample for analysis. 15 elements (Co, Ce, Ca, Mn, Sr, Ba, Li, Rb, U, La, Th, Na, Al, Zr and Hf) were selected to identify manufacturers because some elements (Cu, Cr, Cd and Ni) were below the detection limit and some elements (Ti, Pr, Mg, Nb, Nd) were absent in the analysis of standards and others (Pb and Sn) had a problem of homogeneity. The attempts to identify manufacturers and the manufacturing period were performed through a triangular diagram. In the manufacturer discrimination by discriminant analysis, a canonical discriminant function was made based on Mn, Ce and Rb, and each sample could be identified.

요 약: 제조 공장의 구분이 가능한지 검토하기 위하여 LA-ICP-MS를 이용한 한국 자동차 전면 유리의 미량원소 분석을 실시하였다. 먼저 Si를 내부 표준물질로 하여 표준품 NIST 610, 612, 614과 616을 분석하여 검량선을 작성하였다. 시료와 표준품은 24원소에 대해 정량을 실시하였고 LOQ는 0.11 mg/kg(Ti)-4.91 mg/kg(Ca) 였다. 2개 공장의 11개 시료에 대하여 각각 5개씩의 위치에 따른 부시료를 분석하였다. 검출한계이하의 원소들(Cu, Cr, Cd와 Ni), 표준품에 존재하지 않는 원소들(Ti, Pr, Mg, Nb, Nd)과 균질성에 문제가 있는 원소들(Pb와 Sn)은 분석 대상 원소에서 제외하였다. 제조공장과 제조년도와 관련하여 삼각 다이어그램을 그려 본 결과 구별의 가능성을 볼 수 있었으며 Mn, Ce와 Rb를 토대로 한 정준 판별 분석식에 의해 제조공장의 구별이 가능하였다.

Key words : LA-ICP/MS, glass, forensic chemistry, discriminantion, element

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1. Introduction

Glass debris can be created by a hit-and-run car accident, a burglary, an assault, a drive-by shooting, and an explosion. Many methods are used to classify and discriminate glass because the debris can give important clues for the police.[1] Mechanical and optical properties such as color, thickness and refractive index are primarily used for classification, but recently there are limits in classification because of only slight changes in the refractive index due to improved quality management in the glass factory leading to a more constant product. The elemental composition of glass is known to be important in classification.[2]

There are many methods used for the elemental analysis of glass. AAS (Atomic Absorption Spectroscopy), XRF (X-ray Fluorescence), EDS/WDS (Energy Dispersive Spectroscopy/Wavelength Dispersive Spectroscopy), Electron microscopy, NAA (Neutron Activation Analysis), ICP/AES (Inductively Coupled Plasma/Atomic Emission Spectroscopy) and ICP-MS (Inductively coupled plasma mass spectrometry) can be used. Each method has strong points and weak points, but it is reported that ICP-MS is the most effective in the elemental analysis of glass debris.[3] Compared to other methods, ICP-MS can perform analyses on major elements and trace elements simultaneously, can handle many elements in a unit time due to short analysis time, and can provide information on isotope compositions as well.

In addition, if laser ablation is used for sampling, a very small sample is necessary because there is no need of pretreatment such as dissolution of samples, and the analysis is made in a micro range (size below mm scale). Therefore, it is almost the nondestructive analysis. Furthermore, it is estimated that the LA-ICP-MS is very useful in the analysis of glass debris for forensic applications.

The LA-ICP-MS is used widely in the analysis of elements and isotopes in many samples, but there are few reports on forensic applications of the produced data.[4] In order to establish an analysis method, thorough reviews on sample homogeneity, reproducibility of analysis, precision and accuracy in glass analysis, and precision for classification and discrimination of glass debris are necessary. In this paper, elemental analyses were made of car glass from the KCC Corporation and HanGlass among Korean car glass manufacturers, and elements were sought for classifying between the two manufacturers and manufacturing period for each manufacturer.

2. Materials and Methods

2.1. Samples and sampling method

Six products from HanGlass and five products from KCC Corporation were used in this study, and manufacturing dates for all samples (except for one sample from HanGlass) were identified. Five sub-samples from each sample were taken and analyzed for sample homogeneity. The size of sub-samples after breaking into pieces was about 5 mm × 5 mm, and their surfaces were made smooth. The surface of each sub-sample was cleaned with methanol-distilled water-1% nitric acid and ultrasonic cleaner, and was then dried before analysis.

2.2. Analysis method

2.2.1. Instruments

The LA-ICP-MS used in this study was an Elan 6000 ICP-MS system of Perkin Elmer with a LSX300 laser ablation unit of Cetac. The laser system was composed of a Nd: YAG laser, sampling chamber, microscope and CCD, and laser beam splitter as shown in *Fig.* 1(a). Laser with 266 nm wavelength was used in this study, and its beam size could be controlled from 25 mm to 500 mm. In addition, its laser intensity, repetition per hour, moving velocity, and distance between lines could be adjusted. When the laser is irradiated on a sample, there would be a high-energy exchange between the laser and surface of the sample, and the sample would be made into a very small aerosol. The created aerosols were transported into the plasma by argon nebulizer gas, where atomization and ionization of the aerosols occurred. *Fig.* 1(b). shows the surface left over after the ablation of a glass sample by a linear irradiation

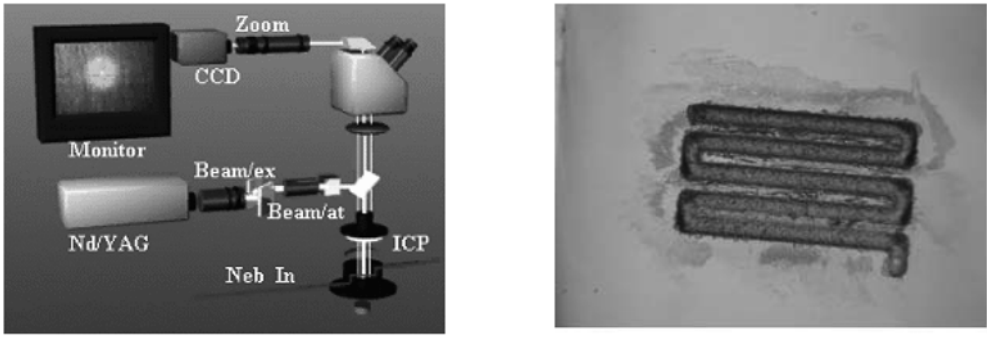

Fig. 1. (a) Nd-YAG Laser system. (b) Surface of glass sample 2-2 after analysis by LA-ICP-MS (The thickness of one line is about 80 μm when the beam size is 100 μm)

Table 1. The condition of LA-ICP/MS

Item	Unit	Value
Crator Diameter	μm	100
Repetition Rate	Hz	10
Laser Output	%	90
Distance between lines	μm	200
Scan speed	μm/sec	20
Nebulizer gas	L/min	0.95
Auxiliary gas	L/min	0.9
Cool gas	L/min	12
RF power	W	1200
Sweeps/Reading		3
Readings/Replicate		30
Replicates		5
Dwell time	ms	10
Scan mode		Peak Hopping

of laser. In the *Fig.* 1(b), the thickness of one line is about 80 mm when the beam size is 100 mm and laser intensity is 100%. The instrument condition of laser and ICP-MS at the time of the glass sample analysis is summarized in *Table* 1.

In this study, 26 elements were analyzed from Al to Zr that were selected because they can be detected with high intensity after ablation by laser. As shown in *Fig.* 1(b), five sub-samples collected 5 different places (upper right, upper left, center, lower right and lower left) on the same pane were sampled at the area of 1 mm × 1 mm size and their average element concentration was used as the concentration of one sample, which is equivalent to averaging whole samples.

After the power of plasma and laser unit was turned on and operation program was initiated, NIST 612 (40 ppm) standard was added into a sampling chamber. While the standards were ablated continuously, sampling gas, lens voltage and plasma position were controlled for optimization to maximize signals of 59Co. 139La, and 208Pb and minimize Ca^{2+} and ThO^{+}/Th ratio. All samples are measured at the same to the standard's condition including laser ablation method.

2.2.2. Quantification of element concentration

The several methods are reported in quantification using LA-ICP-MS, which includes preparing a calibration curve with solution, verifying calibration solution and response correlation between solution and laser, external calibration using solid standard materials, and joint use of external calibration and internal standard.[5] NIST SRM 610 (400 ppm level), 612, 614 and 616 (0.2 ppm level) are used for glass standard using external calibration method. External calibration alone cannot overcome fluctuations in ablation resulting from changes in laser intensity due to small differences on the surface; internal standards must be used together for quantification. Major elements such as Si, Ca and Na can be used for internal standards, but elements other than Si must be measured in advance by other method (e.g., EPMA) because differences in concentration between the sample and the standard must be known. It is reported that there is no

Table 2. The element concentration of glass samples

No. SA	1-1	1-2	1-3	1-4	1-5	Mean	std	%RSD	2-1	2-2	2-3	2-4	2-5	Mean	std	%RSD
Co	1.12	0.98	0.96	1.07	1.01	1.03	0.07	6	6.57	7.37	7.31	7.30	7.35	7.18	0.34	5
Ce	4.41	4.83	5.02	5.00	4.96	4.84	0.25	5	5.56	5.52	5.41	5.33	5.40	5.44	0.09	2
Pb	2.98	1.38	2.54	4.52	3.27	2.94	1.14	39	16.88	1.71	1.77	2.47	2.14	4.99	6.65	133
Ca	54234	65302	63582	66068	67161	63269	5216	8	73880	74877	71713	71565	73456	73098	1429	2
Cu	<0.34	<0.34	<0.34	<0.34	<0.34				<0.34	<0.34	<0.34	<0.34	<0.34			
Mn	20.74	20.28	21.13	21.98	21.69	21.16	0.69	3	29.99	29.87	29.48	29.89	29.93	29.83	0.20	1
Ni	<4.2	<4.2	<4.2	<4.2	<4.2				<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	41.52	49.79	48.73	50.54	50.98	48.31	3.89	8	54.13	53.97	51.96	52.07	52.48	52.92	1.05	2
Ba	77.16	93.36	92.60	94.56	95.77	90.69	7.66	8	138.82	98.03	95.45	95.23	95.84	104.68	19.12	18
Cd	<2.1	<2.1	<2.1	<2.1	<2.1				<2.1	<2.1	<2.1	<2.1	<2.1			
Li	3.92	4.22	4.03	4.21	3.96	4.07	0.14	3	4.07	4.16	3.74	4.04	3.79	3.96	0.19	5
Mg	9904	10282	11519	11645	11935	11057	903	8	12994	13012	12550	12509	12821	12777	239	2
Rb	12.23	13.52	14.26	14.13	14.48	13.72	0.91	7	14.23	14.23	14.63	15.73	15.00	14.76	0.63	4
U	0.92	0.73	0.80	0.70	0.73	0.78	0.09	11	0.69	0.71	0.74	0.76	0.69	0.72	0.03	4
La	2.73	3.03	3.19	3.11	3.15	3.04	0.18	6	3.57	3.59	3.43	3.41	3.45	3.49	0.08	2
Sn	10.24		11.25	11.54	11.32	11.08	0.58	5	1425	26	25	23	23	305	626	206
Th	2.28	2.42	2.41	2.45	2.50	2.41	0.08	3	2.61	2.61	2.55	2.53	2.54	2.57	0.04	1
Na	86439	92469	99112	99280	102127	95886	6360	7	100280	102375	103217	111428	107951	105050	4538	4
Al	4180	5038	4856	5128	5198	4880	412	8	5912	5864	5548	5567	5736	5725	167	3
Ti	113	149	145	152	153	143	17	12	171	171	161	161	165	166	5	3
Cr	5.27	8.21	6.29	7.25	7.13	6.83	1.10	16	8.64	9.03	8.04	6.47	7.09	7.85	1.07	14
Zr	47.61	59.73	57.77	61.20	62.17	57.70	5.88	10	66.32	67.92	63.69	63.59	65.55	65.41	1.83	3
Nb	3.87	3.92	3.96	3.94	3.92	3.92	0.03	1	3.94	3.95	3.94	3.92	3.91	3.93	0.02	0
Hf	3.20	3.54	3.47	3.58	3.59	3.48	0.16	5	3.68	3.69	3.61	3.62	3.65	3.65	0.04	1
Pr	2.75	2.84	2.78	2.77	2.80	2.79	0.03	1	2.88	2.87	2.83	2.84	2.81	2.85	0.03	1
Nd	<1.7	<1.7	<1.7	<1.7	<1.7				<1.7	<1.7	<1.7	<1.7	<1.7			

No. SA	3-1	3-2	3-3	3-4	3-5	Mean	std	%RSD	4-1	4-2	4-3	4-4	4-5	Mean	std	%RSD
Co	2.31	2.44	2.42	2.16	1.99	2.26	0.19	8	6.06	7.23	7.89	8.16	5.41	6.95	1.18	17
Ce	6.96	7.05	7.48	8.58	7.45	7.50	0.65	9	10.26	6.98	7.81	10.23	8.01	8.66	1.50	17
Pb	0.91	-0.20	0.30	2.84	0.07	0.78	1.22	156	2.33	2.76	3.22	1.52	0.64	2.09	1.03	49
Ca	65501	74227	75692	81020	80684	75425	6304	8	63653	48231	59058	59228	66420	59318	6932	12
Cu	<0.34	<0.34	<0.34	<0.34	<0.34				<0.34	<0.34	<0.34	<0.34	<0.34			
Mn	102.50	104.76	110.26	114.14	109.54	108.24	4.63	4	32.63	25.11	28.94	30.02	31.56	29.65	2.90	10
Ni	<4.2	<4.2	<4.2	<4.2	<4.2				<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	53.23	56.05	60.38	63.99	60.37	58.80	4.20	7	44.88	37.55	43.78	43.22	46.71	43.23	3.44	8
Ba	38.86	37.22	43.05	46.32	39.78	41.05	3.64	9	80.25	69.35	84.07	74.18	86.03	78.77	6.94	9
Cd	<2.1	<2.1	<2.1	<2.1	<2.1				<2.1	<2.1	<2.1	<2.1	<2.1			
Li	5.72	5.52	5.80	5.84	5.72	5.72	0.13	2	9.47	8.52	8.92	8.80	9.62	9.07	0.46	5
Mg	13144	14731	14726	14549	15475	14525	851	6	15926	11697	14203	14252	16468	14509	1865	13
Rb	12.70	10.05	13.67	12.92	10.51	11.97	1.59	13	12.23	11.64	12.70	11.91	12.93	12.28	0.54	4
U	1.62	1.65	1.64	1.66	1.68	1.65	0.02	1	2.03	1.96	1.99	1.98	1.97	1.99	0.03	1
La	3.85	4.02	4.22	4.50	4.41	4.20	0.27	6	3.85	3.48	3.82	3.84	3.92	3.78	0.17	5
Sn	1715.16	43.94	43.11	1963.78	2453.54	1243.91	1127.54	91	5227.45	34.33	43.45	41.796	15.14	2272.43	3069.74	135
Th	2.42	2.50	2.57	2.60	2.61	2.54	0.08	3	3.48	3.40	3.54	3.54	3.56	3.51	0.06	2
Na	105881	108472	112339	105289	111415	108679	3172	3	115613	105920	116294	115553	120667	114810	5402	5
Al	8990	10203	10302	11234	11199	10386	918	9	5938	5008	6033	5817	6697	5899	603	10
Ti	362	343	421	457	377	392	46	12	171	126	160	162	178	159	20	13
Cr	8.29	9.73	8.71	15.69	12.13	10.91	3.06	28	<0.1	<0.1	<0.1	<0.1	2.74	2.74		

Table 2. Continued.

No. SA	1-1	1-2	1-3	1-4	1-5	Mean	std	%RSD	2-1	2-2	2-3	2-4	2-5	Mean	std	%RSD
Zr	104.20	106.12	123.87	134.59	119.06	117.57	12.67	11	51.76	42.70	52.52	55.92	54.67	51.52	5.20	10
Nb	4.03	3.90	4.06	4.13	3.97	4.02	0.09	2	9.27	9.12	9.23	9.23	9.26	9.22	0.06	1
Hf	4.58	4.55	4.93	5.27	4.89	4.84	0.29	6	6.07	5.90	6.18	6.22	6.09	6.09	0.12	2
Pr	3.17	3.18	3.27	3.36	3.29	3.25	0.08	3	6.91	6.79	6.85	6.87	6.87	6.86	0.04	1
Nd	<1.7	<1.7	<1.7	<1.7	<1.7				3.18	2.92	3.19	3.12	3.32	3.15	0.15	5

	5-1	5-2	5-3	5-4	5-5	Mean	std	%RSD	6-1	6-2	6-3	6-4	6-5	Mean	std	%RSD
Co	5.74	5.81	6.07	4.70	4.47	5.36	0.72	13	4.25	4.53	6.43	4.61	5.07	4.98	0.86	17
Ce	6.86	7.28	8.32	9.03	9.22	8.14	1.04	13	6.80	6.84	6.71	7.34	7.58	7.06	0.38	5
Pb	1.77	0.71	1.72	0.41	0.40	1.00	0.69	69	0.73	0.44	0.14	0.77	0.78	0.57	0.28	49
Ca	61981	60337	67529	72565	72312	66945	5680	8	71010	73228	66211	79069	78754	73655	5429	7
Cu	<0.34	<0.34	<0.34	<0.34	<0.34				<0.34	<0.34	<0.34	<0.34	<0.34			
Mn	83.77	85.11	97.79	109.01	108.78	96.89	12.25	13	56.76	55.10	54.00	59.48	61.64	57.40	3.15	5
Ni	<4.2	<4.2	<4.2	<4.2	<4.2				<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	45.80	47.65	56.10	61.41	61.81	54.56	7.52	14	25.42	25.59	24.80	27.52	28.00	26.27	1.40	5
Ba	21.40	20.11	24.71	27.61	28.25	24.42	3.63	15	20.32	17.53	15.97	21.87	21.38	19.41	2.56	13
Cd	<2.1	<2.1	<2.1	<2.1	<2.1				<2.1	<2.1	<2.1	<2.1	<2.1			
Li	10.87	11.33	12.37	13.68	14.04	12.46	1.40	11	8.22	8.50	8.14	8.95	9.11	8.58	0.43	5
Mg	16944	16329	18127	19480	19439	18064	1429	8	15516	15516	14366	16491	16968	15771	1007	6
Rb	13.19	14.49	16.30	17.66	17.28	15.78	1.90	12	4.79	4.84	4.71	5.32	5.56	5.04	0.37	7
U	2.14	2.21	2.36	2.47	2.47	2.33	0.15	6	1.87	1.85	1.84	1.87	1.90	1.87	0.02	1
La	3.92	3.97	4.49	4.79	4.78	4.39	0.42	10	4.62	4.72	4.54	4.98	5.03	4.78	0.22	5
Sn	14.01	13.60	19.12	3294.09	3187.36	1305.64	1766.89	135	1811.49	1701.10	13.27	1870.10	1688.73	1416.94	788.34	56
Th	3.71	3.81	4.14	4.36	4.42	4.09	0.32	8	3.72	3.73	3.70	3.85	3.87	3.78	0.08	2
Na	104977	108719	119397	128881	124019	117199	10113	9	87988	85749	91087	95593	103838	92851	7167	8
Al	13668	12654	14092	11700	11290	12681	1211	10	6740	6838	6259	7217	7119	6835	377	6
Ti	260	251	295	319	320	289	32	11	180	178	165	192	194	182	12	6
Cr	<0.1	<0.1	<0.1	<0.1	0.94	0.94			<0.1	<0.1	<0.1	<0.1	<0.1			
Zr	36.20	36.70	44.44	49.51	48.78	43.13	6.40	15	36.79	37.84	36.52	41.78	42.12	39.01	2.73	7
Nb	10.01	10.03	10.27	10.43	10.38	10.22	0.20	2	9.07	9.09	9.01	9.12	9.09	9.08	0.04	0
Hf	5.49	5.55	5.80	5.99	5.99	5.76	0.24	4	5.46	5.45	5.40	5.55	5.51	5.47	0.05	1
Pr	6.88	6.91	7.03	7.08	7.12	7.00	0.10	1	6.91	6.93	6.89	6.97	6.98	6.94	0.04	1
Nd	3.45	3.47	3.97	4.33	4.31	3.91	0.43	11	3.49	3.56	3.39	3.70	3.70	3.57	0.14	4

	7-1	7-2	7-3	7-4	7-5	Mean	std	%RSD	8-1	8-2	8-3	8-4	8-5	Mean	std	%RSD
Co	7.87	6.55	7.90	7.71	7.17	7.44	0.58	8	7.29	6.35	7.06	6.13	5.98	6.56	0.58	9
Ce	8.66	9.73	9.12	8.93	8.37	8.96	0.51	6	4.50	4.87	4.41	4.70	4.81	4.66	0.20	4
Pb	3.04	8.76	7.35	6.69	4.44	6.06	2.30	38	3.06	1.43	1.78	1.46	1.54	1.86	0.69	37
Ca	65789	76851	68414	65579	57644	66855	6891	10	76370	80262	58864	69216	67381	70418	8314	12
Cu	<0.34	<0.34	<0.34	<0.34	<0.34				<0.34	<0.34	<0.34	<0.34	<0.34			
Mn	36.16	40.13	37.03	35.65	32.35	36.26	2.79	8	56.79	66.47	53.95	60.42	57.06	58.94	4.79	8
Ni	<4.2	<4.2	<4.2	<4.2	<4.2				<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	43.83	50.09	46.72	45.04	40.90	45.32	3.41	8	46.85	56.58	44.48	50.92	49.66	49.70	4.59	9
Ba	76.07	82.52	84.40	88.75	72.44	80.83	6.54	8	71.87	85.57	67.06	79.05	75.69	75.85	7.04	9
Cd	<2.1	<2.1	<2.1	<2.1	<2.1				<2.1	<2.1	<2.1	<2.1	<2.1			
Li	11.72	13.18	12.33	12.58	12.21	12.40	0.53	4	10.12	11.15	10.46	11.90	11.93	11.11	0.82	7
Mg	14275	16950	14944	14419	12983	14714	1443	10	13641	17197	12867	15612	14904	14844	1695	11
Rb	12.55	13.85	13.26	12.63	12.22	12.90	0.65	5	15.42	18.25	15.90	17.77	17.52	16.97	1.24	7

Table 2. Continued.

No. SA	1-1	1-2	1-3	1-4	1-5	Mean	std	%RSD	2-1	2-2	2-3	2-4	2-5	Mean	std	%RSD
U	2.14	2.20	2.19	2.22	2.18	2.19	0.03	1	1.95	1.98	1.96	1.99	1.96	1.97	0.02	1
La	5.57	6.15	5.88	5.78	5.29	5.74	0.32	6	3.36	3.70	3.29	3.46	3.42	3.45	0.16	5
Sn	27.283	861.53	27.34	27.12	24.06	793.46	1715.10	216	28.46	4730.20	31.314	452.505	249.38	2898.372	634.13	91
Th	4.50	4.77	4.79	4.80	4.58	4.69	0.14	3	3.31	3.41	3.30	3.37	3.38	3.36	0.05	1
Na	106890	118356	114782	113639	109370	112607	4528	4	100331	116461	103098	115675	112914	109696	7468	7
Al	6355	6758	6171	5876	5148	6061	603	10	9445	9610	8441	8132	8028	8731	745	9
Ti	190	228	205	193	171	197	21	11	90	179	115	156	149	138	35	25
Cr	<0.1	<0.1	<0.1	<0.1	<0.1				<0.1	<0.1	<0.1	<0.1	<0.1			
Zr	47.80	51.26	52.11	49.62	42.98	48.75	3.62	7	28.73	34.74	24.91	29.03	29.23	29.33	3.51	12
Nb	9.34	9.45	9.37	9.33	9.24	9.35	0.08	1	9.05	9.13	9.00	9.05	9.04	9.05	0.05	1
Hf	5.93	6.04	6.10	6.09	5.94	6.02	0.08	1	5.57	5.71	5.53	5.62	5.66	5.62	0.07	1
Pr	7.18	7.28	7.24	7.22	7.13	7.21	0.06	1	6.76	6.81	6.72	6.74	6.75	6.76	0.03	0
Nd	4.54	5.09	4.81	4.74	4.37	4.71	0.27	6	2.71	2.91	2.67	2.77	2.91	2.80	0.11	4

	9-1	9-2	9-3	9-4	9-5	Mean	std	%RSD	10-1	10-2	10-3	10-4	10-5	Mean	std	%RSD
Co	3.74	3.69	3.79	3.77	3.68	3.73	0.05	1	7.88	8.03	8.67	2.52	2.36	5.89	3.17	54
Ce	71.38	95.24	71.51	92.66	70.37	80.23	12.56	16	9.45	9.68	9.03	8.88	8.73	9.15	0.40	4
Pb	4.12	5.58	3.40	5.27	3.11	4.30	1.10	26	5.69	8.96	4.17	-0.36	-0.54	3.58	4.07	114
Ca	69846	65137	64733	67006	62324	65809	2806	4	61673	63235	64866	66324	66132	64446	1981	3
Cu	<0.34	<0.34	<0.34	<0.34	<0.34				<0.34	<0.34	<0.34	<0.34	<0.34			
Mn	191.69	206.21	184.03	197.36	183.17	192.49	9.63	5	34.33	35.27	29.66	33.76	35.09	33.62	2.30	7
Ni	<4.2	<4.2	<4.2	<4.2	<4.2				<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	51.19	51.47	49.21	52.09	48.60	50.51	1.52	3	58.41	60.29	46.02	53.92	54.28	54.58	5.50	10
Ba	135.68	144.48	128.07	143.74	126.46	135.68	8.44	6	128.02	133.88	89.64	109.14	107.33	113.60	17.69	16
Cd	<2.1	<2.1	<2.1	<2.1	<2.1				<2.1	<2.1	<2.1	<2.1	<2.1			
Li	16.57	18.61	16.28	18.67	16.59	17.35	1.19	7	4.22	4.21	9.48	5.50	6.46	5.98	2.18	36
Mg	13520	13933	13175	14896	13545	13814	662	5	11019	11050	10407	10659	10630	10753	275	3
Rb	18.26	20.93	18.10	20.72	17.95	19.19	1.50	8	18.09	18.69	14.79	14.28	14.42	16.05	2.15	13
U	2.57	2.64	2.62	2.56	2.50	2.58	0.05	2	1.42	1.43	2.31	1.43	1.50	1.62	0.39	24
La	7.65	7.79	7.56	7.72	7.30	7.60	0.19	2	3.49	3.53	3.98	3.18	3.26	3.49	0.31	9
Sn	9.843	342.47	17.94	3020.07	18.68	1281.80	1737.72	136	70.70	73.72	33.299	335.248	963.40	3695.274	980.60	135
Th	4.54	4.52	4.47	4.46	4.43	4.48	0.04	1	2.53	2.56	3.68	2.65	2.61	2.81	0.49	18
Na	93055	107187	95257	109005	97460	100393	7231	7	114149	116320		95287	95720	105369	11427	11
Al	10933	11785	10719	11062	11030	11106	402	4	6344	6658	5219	6375	6572	6234	582	9
Ti	267	301	251	308	276	281	24	8	234	276	116	215	216	211	59	28
Cr	12.22	42.31	16.78	56.26	34.01	32.32	18.18	56	<0.1	1.18	<0.1	64.82	68.18	44.73	37.75	84
Zr	42.20	41.64	40.72	40.81	39.78	41.03	0.93	2	76.92	79.69	54.29	67.42	68.43	69.35	9.94	14
Nb	9.42	9.54	9.40	9.45	9.36	9.43	0.07	1	2.59	2.57	9.43	2.91	2.82	4.06	3.00	74
Hf	6.12	6.13	6.08	6.09	6.03	6.09	0.04	1	4.43	4.48	6.41	4.48	4.44	4.85	0.87	18
Pr	7.63	7.74	7.54	7.62	7.52	7.61	0.08	1	2.70	2.63	7.07	2.69	2.64	3.54	1.97	56
Nd	5.74	5.01	5.53	5.46	5.49	5.45	0.27	5	2.17	2.37	3.39	2.36	2.15	2.49	0.51	21

	11-1	11-2	11-4	11-3	11-5	Mean	Std	%RSD
Co	2.19	7.54	7.26	1.99	1.90	4.18	2.95	71
Ce	11.65	12.77	12.13	11.91	11.74	12.04	0.45	4
Pb	0.72	<0.07	<0.07	73.80	101.26	58.60	51.97	89
Ca	80262	70161	68865	91257	84184	78946	9481	12
Cu	0.62	<0.34	<0.34	25.11	20.22			

Table 2. Continued

No. SA	1-1	1-2	1-3	1-4	1-5	Mean	std	%RSD
Mn	93.08	85.24	83.80	80.96	87.08	86.03	4.53	5
Ni	<4.2	<4.2	<4.2	<4.2	<4.2			
Sr	42.98	40.81	40.82	49.23	50.05	44.78	4.54	10
Ba	40.29	37.63	37.12	360	576	210	247	118
Cd	<2.1	<2.1	<2.1	<2.1	<2.1			
Li	6.71	7.50	7.67	8.88	8.56	7.86	0.87	11
Mg	11164	10189	10220	10622	10504	10540	395	4
Rb	8.22	10.33	9.89	9.60	9.48	9.50	0.79	8
U	1.53	2.27	1.71	1.54	1.53	1.72	0.32	19
La	6.46	6.40	6.07	6.76	6.55	6.45	0.25	4
Sn	7830.35	43.13	43.94	8754.03	8474.33	5029.16	4563.53	91
Th	4.36	4.24	4.17	4.50	4.47	4.35	0.14	3
Na	95030	117429	118893	89106	90977	102287	14657	14
Al	5525	4888	4833	7330	6802	5876	1136	19
Ti	253	235	240	264	261	250	13	5
Cr	30.92	1.88	1.85	66.82	71.70	34.63	33.80	98
Zr	64.52	58.72	58.10	70.62	65.26	63.45	5.17	8
Nb	2.47	2.71	2.22	3.75	3.80	2.99	0.74	25
Hf	4.31	4.31	4.17	4.65	4.47	4.38	0.18	4
Pr	3.17	3.30	3.20	3.24	3.29	3.24	0.06	2
Nd	4.62	4.59	4.38	4.65	4.64	4.58	0.11	2

problem for Si among various glass samples except typical glass eg. borosilicate, decorative glass, etc.[6] In other words, each element in the standard and the sample is normalized against ^{29}Si, and the element concentration for each sample is calculated using a linearity of concentration. The results are summarized in *Table* 2.

2.2.3. Statistical analysis of data

For classification and discrimination according to products, various statistical analyses are necessary. Since 11 samples from two manufacturers and five sub-samples for each sample were used in this study, linear discriminant analysis was employed for identification according to a manufacturer. The classification according to manufacturing period for each manufacturer was performed through a triangular diagram using three elements. The discrimination analysis for classification according to manufacturing period was difficult due to the small number of samples for each period. SPSS 12.0v and Excel programs were used for statistical analysis.[7]

3. Results and Discussion

3.1. The limit of detection (LOD) and external calibration curve

The signal of each element is measured while the surface of the sample is not irradiated when the laser is turned on, and its standard deviation is calculated. The LOD and the LOQ are calculated by the following equation by measuring signals of each element on NIST 612 (40 ppm level).

$$LOD(mg/kg) = \frac{3 \times I(std)_{bark}}{I(mean)_{=ST612}} \times Conc_{=ST612}$$

The LOQ was calculated by multiplying the LOD by 3.3. The representative LODs and LOQ obtained in this study are summarized in *Table* 3. The LOQs are varied according to elements, but it was in the range of 0.04 mg/kg (Sr) to 4.91 mg/kg (Ca).

Table 3. The LOD and the LOQ

Element	Limit of detection, LOD, mg/kg	Limit of quantification LOQ, mg/kg
Al	0.13	0.44
Ba	0.04	0.15
Ca	1.49	4.91
Cd	0.66	2.16
Ce	0.13	0.44
Co	0.10	0.34
Cr	0.03	0.10
Cu	0.10	0.34
Hf	0.33	1.10
La	0.26	0.86
Li	1.00	3.30
Mg	0.10	0.34
Mn	0.14	0.47
Na	0.08	0.25
Nb	0.25	0.84
Nd	0.52	1.73
Ni	1.28	4.24
Pb	0.02	0.07
Pr	0.16	0.53
Rb	0.27	0.88
Sn	0.22	0.74
Sr	0.01	0.04
Th	0.12	0.40
Ti	0.03	0.11
U	0.10	0.33
Zr	0.17	0.55

Table 4. External calibration curve data for Sr. Signal ratio of Sr/Si and concentration in standard material

Glass, NIST	Sr/Si	Sr/Si standard deviation	Sr/Si	Sr/Si standard deviation	Sr/Si	Sr/Si standard deviation	Reported concentration Sr in $mgkg^{-1}$, [Sr]	[Sr] uncertqinty, in $mgkg^{-1}$
616	0.03747	0.00339			0.06058	0.00001	41.72	
614	0.04014	0.00131	0.05487	0.00212	0.06692	0.00268	45.8	
612	0.06641	0.00294	0.08519	0.00292	0.11133	0.00437	76.15	2.29
610	0.29256	0.00587	0.65261	0.01558	0.80922	0.04144	467.4	18.3

In this study three calibration curves were obtained using NIST 616, 614, 612 and 610. The referred values used were those collected and recommended by Pearce *et al*.,[8] and those certified and published by NIST. Therefore, in the case of NIST 612 and 610, there are certified values based on standard materials for all elements analyzed, but there are cases in which the certified values of NIST 614 and 616 are absent. For example, *Table* 4 and *Fig.* 2 present a recommended concentration for Sr and measured ratio of Sr/Si, which are drawn in the figure with a regression equation and correlation coefficients. The concentration vs. element/Si signal ratio in the standard materials shows a good linear relation, and its slope changes significantly according to measurement date. That is to say, the LOD is varied significantly according to instrument conditions.

3.2. Reproducibility using a standard material

NIST 612 is measured after every 5~8 sample analyses for eight analyses and the variation of elemental concentrations in NIST 612 is shown in *Fig.* 3 and 4. The elemental concentration should yield the same value even though the slope of the calibration curve would be changed. For most elements, it changes within 10% compared to the certified value, but Mg, Nb and Nd in *Fig.* 3 and Ti and Pr in *Fig.* 4 show that the determined concentrations change significantly. In other words, the internal standard Si and metals do not always change consistently. Therefore, data for Mg, Nb, Nd, Ti, and Pr were not used in statistical analysis in the real samples.

3.3. Homogeneity of samples

Five sub-samples for each sample were analyzed

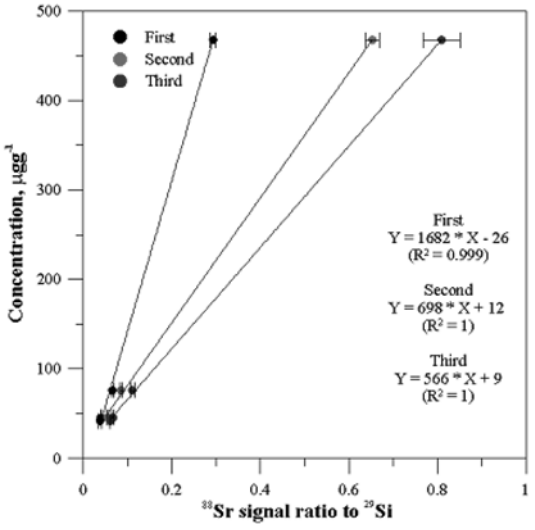

Fig. 2. The comparison of three calibration curves of Sr.

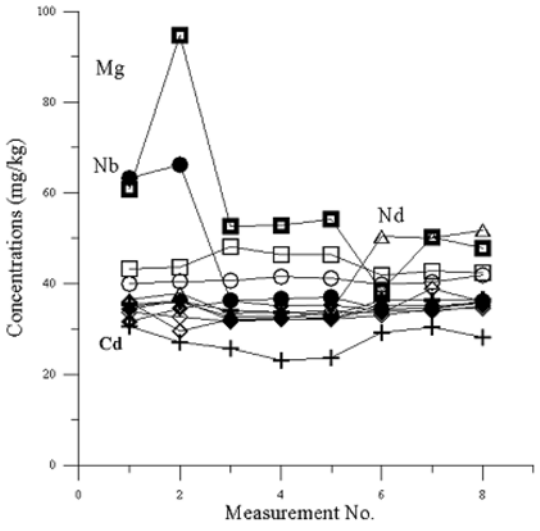

Fig. 3. Data obtained by eight analyses on NIST 612. Changes in Mg, Nb and Nd are large.

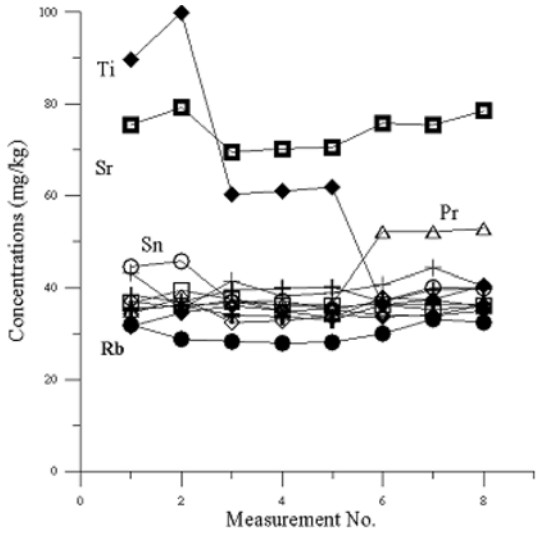

Fig. 4. Data obtained by eight analyses on NIST 612. Changes in Ti and Pr are large.

and average values and standard deviations of them (except for samples below the LOD) were obtained and summarized in *Table* 3. Elements with more than 10% of relative standard deviation for all samples in average were Co, Pb, Ba and Ti, and the standard deviation of Pb, in particular, was as high as 76%. This is assumed to result from the incomplete washing of Pb from the glass surface, and suggests the use of hydrochloric acid rather than nitric acid for washing in the future. Co, Ba and Ti show 12~16% of deviation range and sample 10 has large fluctuation. Other elements show deviations within 10%, which indicates homogeneous distribution of elements. Therefore, in the coming classification and discrimination of products, metals other than elements below detection limit (Cu, Cr, Cd and Ni), elements with problems in the analysis of standards (Ti, Pr, Mg, Nb, Nd) and elements with problems in homogeneity (Pb and Sn) were selected for analysis. Especially, Sn is in high concentration in one surface and low concentration in the other surface in float glasses.

3.4. Identification of manufacturers

Concentration of elements analyzed for each sample is summarized in the *Table* 2. Concentrations of Mn and Co obtained from each sample are listed in *Fig.* 5, along with their manufacturers. The patterns of Mn and Co in the 5 sub-samples are very similar to one another, which indicates that all samples are homogeneous for the elements. The change of concentrations of Mn is very wide, ranging from 20 mg/kg to 200 mg/kg, and that of Co is also very wide ranging from about 1 mg/kg to 8 mg/kg within whole samples. When the concentration of Mn is analyzed for the same manufacturer, the changes of concentration of Mn are small, ranging 20-50 mg/kg for glasses from HK, whereas those of Mn is large ranging 50-200 mg/kg for glasses from KK. In case of Co, the concentration ranges 1-8 mg/kg for glasses from HK, and 2-6 mg/kg for glasses from KK. Therefore, when discrimination is attempted between the manufacturers, Mn gives relatively better discrimination than Co, which has an overlapping range. It is therefore recommended to perform multivariate analysis considering several elements together.

There are several modes of classification and discrimination in the multivariate analysis, and unknown samples can be classified through a canonical discrimination function by linear discriminant analysis.

In the discriminant analysis by SPSS 12.0v, analyzed elements were assigned to independent variables,

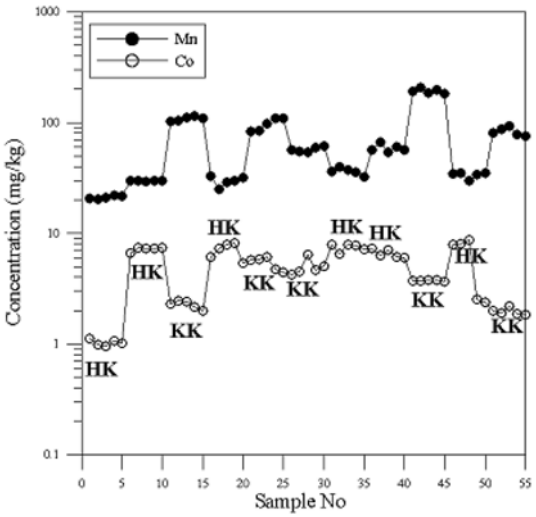

Fig. 5. Concentration of Mn and Co for all samples analyzed. HK and KK represent manufacturers.

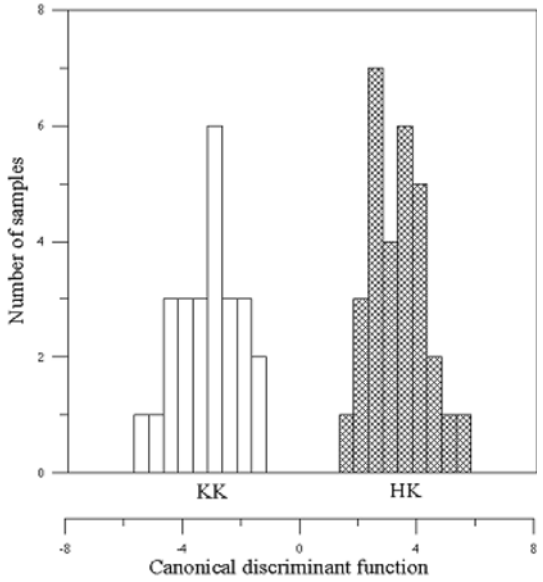

Fig. 6. Histogram of glass samples according to canonical discrimination function. It shows a clear discrimination between samples of KK and HK.

and a group was assigned to dependent variables. Elements other than the previously discussed (Cu and Sn) were determined by a stepwise variable selection. According to the discriminant analysis, a canonical discrimination function was made by three elements of Ce, Mn and Rb. The eigenvalue was 10.78 and can explain 91.6% of all variables (canonical correlation coefficient 0.957). The canonical discrimination function made of three elements is shown below, and the obtained value for glasses of HK was 3.02±0.921 (N=30) and that for glasses of KK was -3.47±1.081 (N=25) according to the function.

A histogram made by applying each sample using the discrimination function is shown in *Fig.* 6. The X-axis means discriminant score. All samples can be discriminated into two groups as expected, and those belonging to KK are on the left side, while those belonging to HK are on the right of the figure.

2.5. Discrimination by manufacturing period

If the number of samples for each period is enough (20 samples per group), the discriminant analysis according to the manufacturing period is possible. In this study, there are only five samples for each period,

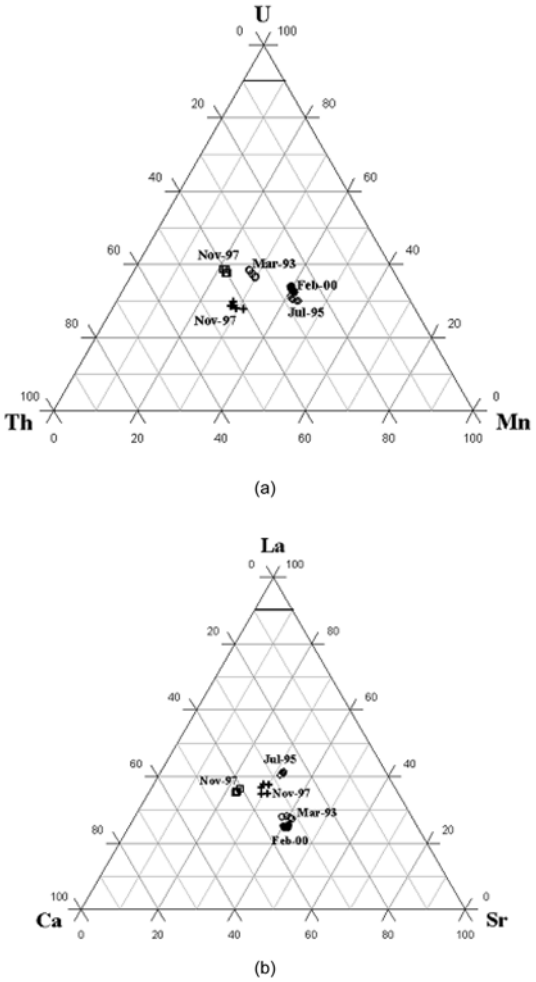

Fig. 7. Discrimination by manufacturing period on glasses of KK according to Mn-Th-U (a) and Sr-Ca-La (b).

and the discriminant analysis has no meaning. Therefore, other methods using a triangular diagram are used for discrimination. In the first case of glasses of KK, the manufacturing periods of Mar-93, Jul-95, Nov-97 (2), and Feb-00 (*Fig.* 7) were clearly separated by a triangular diagram of Mn-U-Th or Sr-La-Ca. The five analysis values according to each period are well separated and are placed at separate points on a triangular diagram. The two samples on Nov-97 are placed on different points on the triangular diagram and show the possibility of different composition according to the manufacturing line, even though they are produced on the same period.

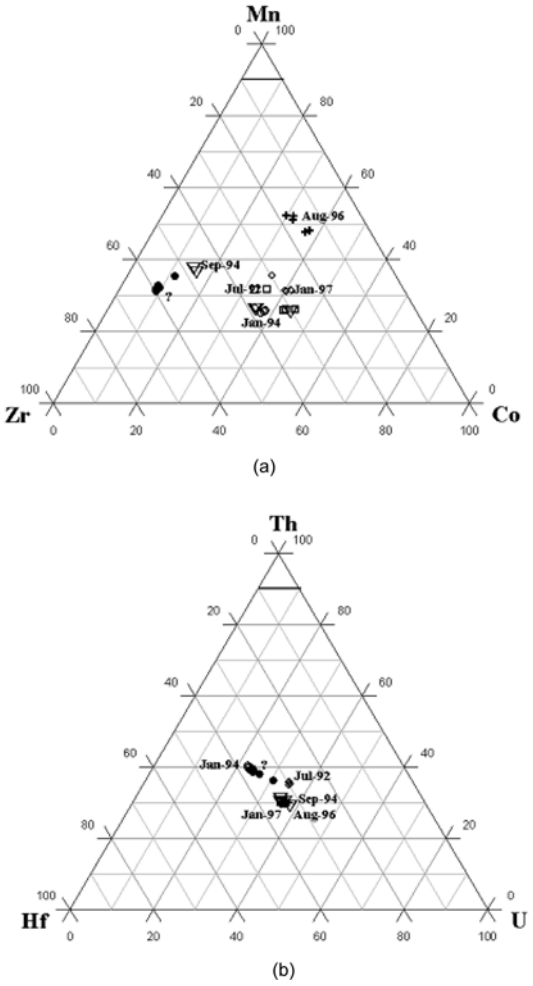

Fig. 8. Discrimination by manufacturing period on glasses of HK according to Th-Hf-U (a) and Mn-Zr-Co (b).

For glasses of HK, attempts were made to discriminate through a triangular diagram of Hf-Th-U or Mn-Zr-Co, but problems in sample homogeneity, especially for Sep-94 and Jul-92, occurred. At ternary plot, each side of the triangle represents a proportion of 0%, with the point of the triangle opposite that base representing a proportion of 100%. As a proportions increases in any one sample, the point representing that sample moves from the base to the opposite point of the triangle. Therefore, a method using more variables with an increased number of samples is sought to allow composition discrimination according to the manufacturing period for glass of HK.

4. Conclusion

The analysis on metallic elements in glass debris using LA-ICP-MS was performed, and attempts were made to identify a manufacturer using a real sample.

At first, a calibration curve was made using standard glass samples of NIST 610 to 616. Si was used as an internal standard, and the signal ratios of metal/Si for each metal were compared with their concentrations. Based on elements in each sample and standard materials, 24 metals were quantitatively analyzed, and the LOQ according to the blank sample was in the range of 0.11 mg/kg (Ti)-4.91 mg/kg (Ca).

Eleven samples from two manufacturers were collected and five sub-samples were taken from each sample for analysis. Using metals other than elements below detection limit (Cu, Cr, Cd and Ni; elements with problems in the analysis of standards (Ti, Pr, Mg, Nb and Nd) and elements with problems in homogeneity (Pb and Sn), attempts were made to identify manufacturers and manufacturing period by a triangular diagram.

In manufacturer discrimination by discriminant analysis, a canonical discrimination function was made based on Mn, Ce and Rb. All investigated samples were correctly identified as being produced by one of these two manufacturers. For glasses of KK, even the manufacturing period could be discriminated using a triangular diagram of Mn-Th-U or Sr-Ca-La. For glasses of HK, due to problems in homogeneity, the discrimination by manufacturing period according to triangular diagram was difficult, and more variables are need for further analysis.

Acknowledgement

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