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A. J. Hebert

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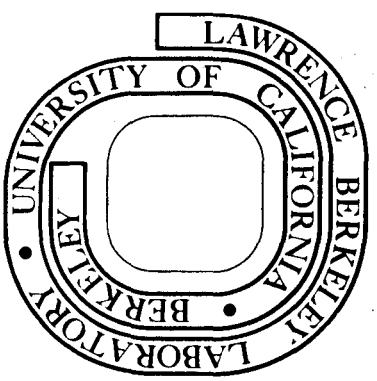

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NON-DISPERSIVE SOFT X-RAY FLUORESCENCE ANALYSES *

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In conventional dispersive X-ray fluorescence analysis, the X-rays of interest are sorted out according to the angles which they make with analyzing crystals. In a non-dispersive system, all X-rays incident on the detector (with little angular dependence) are analyzed according to energy in a time sharing manner.

The spectrometer and techniques I will describe were designed to take advantage of the features of a non-dispersive detector. These include sensitivity, relatively short geometry, and the ability to detect oxygen and sodium X-rays at the low energy end of the elemental scale.[1]

Samples are prepared by first crushing and grinding them to a powder. The weighed sample powder is fused at 900° C. in a platinum crucible with weighed $LiBO_2$, (usually 10/1 $LiBO_2$ to sample) while being stirred with a vitreous carbon rod. The resultant homogeneous liquid is then poured into a ring which is on a vitreous carbon disk. The liquid mass is pressed briefly with a gold foil that has been inlaid in a copper block. Figure 1 shows the press and annealing hot plate with a vitreous carbon disk and a finished glass pill.

Sample rings have been designed to allow scaling down of the usual 300 mg sample to as little as 50 mg. The glass pills can be analyzed repeatedly over periods of years when stored in vacuum dessicators to minimize contamination and moisture pick-up.

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* Work done under the auspices of the U.S Energy Research and Development Administration.

The spectrometer is housed in a 4 in square (10 cm^2) iron vacuum chamber with a multiple sample rotating transfer shaft to take the samples into vacuum and properly reference them. The unit is shown in Figure 2. On top is the anode selector knob which allows six soft X-ray anodes and filters to be selected during the analysis without interruption of the vacuum.

Figure 3 shows the relative positions of the major spectrometer components, and the differential pumping arrangement which allows change of anode or sample without burps or loss of vacuum. The electron gun shown in Figure 4 was designed to give a flux of electrons without contaminating the anodes with surface vaporized species. The rotating anodes shown here are also protected against line of sight sputtering cross contamination. Figure 5 shows a schematic diagram of the spectrometer geometry.

At this point I might mention that the very low power levels incident on the samples (of the order of milliwatts) has allowed the non-destructive analyses of many types of samples which would vaporize in a conventional spectrometer.

Table I lists the various anodes, filters, X-ray energies and the elements which can be analyzed. The spectra observed for a typical fused sample with the six anodes indicated is shown in Figure 6. Table 2 lists some comparisons between results obtained with our soft X-ray spectrometer and conventional wet chemistry. The samples are standard U.S.G.S. rocks.

Results for several samples of "Late Green" and "Turquoise" ware from Siraf are shown in Table 3. We also analyze for chrome at several hundred ppm, and it was not observed here. Sample 5 differs significantly in sodium, magnesium and potassium. These differences are also observed in the neutron activation analyses results for a separate portion of the same sample. The overall major element appearance separates it from the group. Indeed its removal would also benefit the appearance of the standard deviations for the set.

0 0 0 0 4 3 0 7 1 4 1

The two "Turquoise" ware samples differ significantly from the upper group average in their content of Al_2O_3, K_2O, TiO_2 and FeO, and are thus chemically as well as visually separable from the group.

The glaze results are for glaze on a typical "Late Green" sample .

Figure Captions

Figure 1. Molten glass press and annealing hot plate.

Figure 2. The spectrometer.

Figure 3. Major spectrometer components. Reprinted with permission from A. J. Hebert and Kenneth Street Jr., Analytical Chemistry 46, 203 (1974). Copyright by the American Chemical Society.

Figure 4. Electron gun and anodes. Reprinted with permission from A. J. Hebert and Kenneth Street Jr., Analytical Chemistry 46, 203 (1974). Copyright by the American Chemical Society.

Figure 5. Spectrometer geometry.

Figure 6. Spectra of a fused rock sample. Numbers in upper left hand corners are counts full scale per channel, while the lower right-hand corners indicate energy full scale. Reprinted with permission from A. J. Hebert and Kenneth Street Jr., Analytical Chemistry 46, 203 (1974). Copyright by the American Chemical Society.

Reference

1. A. J. Hebert and Kenneth Street Jr., "Non-Dispersive Soft-X-Ray Fluorescence Spectrometer for Quantitative Analysis of the Major Elements in Rocks and Minerals", Analytical Chemistry 46, 203 (1974).

TABLE 1. Anode and filter data.

Anode	Filter Element	Filter Thickness(mm)	X-Ray Energy (keV)	Elements Analyzed
Mg	Mg(K edge)	0.015	1.25	O, F, Na, and L X-rays of some heavier elements
Al	Al(K edge)	0.013	1.49	O, Na, Mg
Si	Si(K edge)	0.015	1.74	O, Na, Mg, Al
Ag	Ag(L edge)	0.001	2.98	Al, Si, P, S, Cl
Ti	Ti(K edge)	0.025	4.51	Si, Cl, K, Ca, Sc
Ni	Ni(K edge)	0.025	7.48	Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe

0 0 0 4 3 0 7 1 4 2

TABLE 2. Major element analyses. Reprinted with permission from A. J. Hebert and K. Street, Jr., Analytical Chemistry 46, 203 (1974). Copyright by the American Chemical Society. A comparison of present XRF results and preferred values for major elements in USGS standard rocks as percent oxide. The numbers in parentheses represent one standard deviation at the last digit for the observed counting statistics.

Sample	Source	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO
G-2	XRF	4.17(5)	0.77(2)	15.26(9)	69.2(2)	4.50(2)	1.98(2)	0.51(1)	2.40(1)
	Preferred Values	4.15	0.77	15.31	69.29	4.51	2.00	0.48	2.38
	Difference	+0.5%	0	-0.3%	-0.1%	-0.2%	-1.3%	+6%	-1.4%
GSP-1	XRF	2.84(5)	0.99(2)	15.02(9)	67.1(2)	5.54(2)	2.08(2)	0.67(1)	3.81(1)
	Preferred Values	2.86	0.95	14.92	67.32	5.52	2.06	0.66	3.82
	Difference	-0.7%	+3.9%	+0.6%	-0.4%	+0.3%	+1.1%	+2%	-0.1%
AGV-1	XRF	4.36(5)	1.51(2)	16.90(9)	59.6(2)	2.93(2)	4.97(2)	1.03(1)	6.03(1)
	Preferred Values	4.32	1.53	16.92	59.10	2.92	4.98	1.05	6.04
	Difference	+0.9%	-1.5%	-0.1%	+0.8%	+0.3%	-0.3%	-2%	+0.6%

0 0 0 0 4 3 0 7 1 4 3

TABLE 3. Chemical analyses of Siraf pottery samples.
(Normalized to 100% after weight loss on fusion)

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO
(Error)	(±.2)	(±.2)	(±.3)	(±.5)	(±.05)	(±.2)	(±.03)	(±.015)	(±.15)
Late Green									
1	2.46	9.2	12.4	50.1	2.99	16.2	.57	.145	5.86
2	1.45	9.0	12.5	49.7	2.36	18.5	.62	.118	5.73
3	1.81	9.3	11.6	47.8	3.33	19.9	.58	.153	5.47
4	1.65	5.6	11.2	45.7	2.67	27.2	.55	.135	5.27
5	.75	16.6	12.0	46.1	1.76	16.1	.54	.115	6.01
6	1.22	6.1	12.8	48.5	3.18	21.6	.61	.149	5.75
Average	1.56	9.3	12.1	48.0	2.72	19.9	.58	.136	5.68
	±.58	±3.9	±.6	±1.8	±.58	±4.1	±.03	±.016	±.27
Turquoise									
	2.12	7.2	13.4	51.2	1.25	17.6	.67	.148	6.29
	2.46	7.5	13.9	49.2	.95	18.3	.68	.146	6.82
Glaze									
	12.2	1.6	4.1	58.8	4.7	8.8	.5	--	6.5

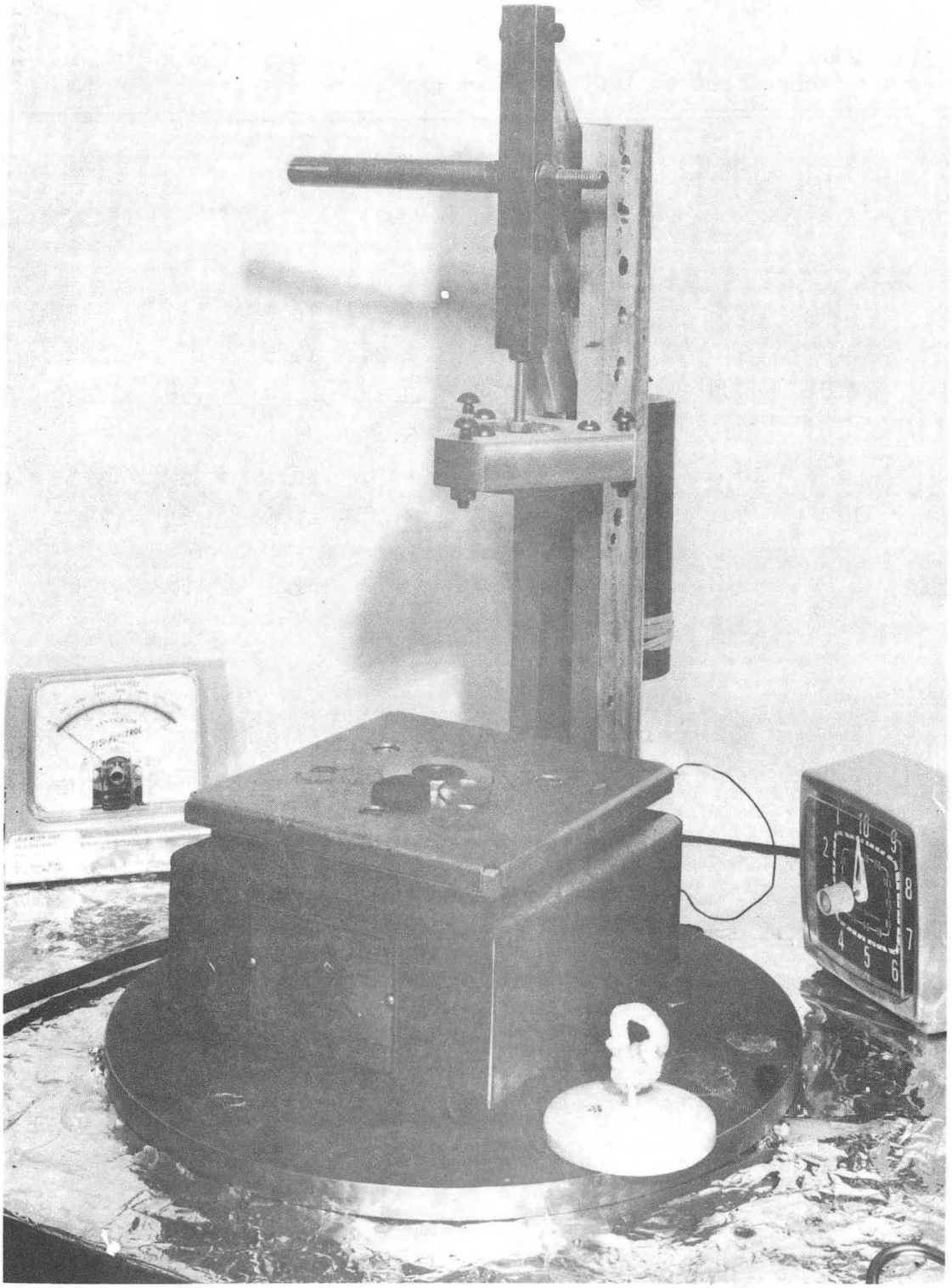

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Fig. 1

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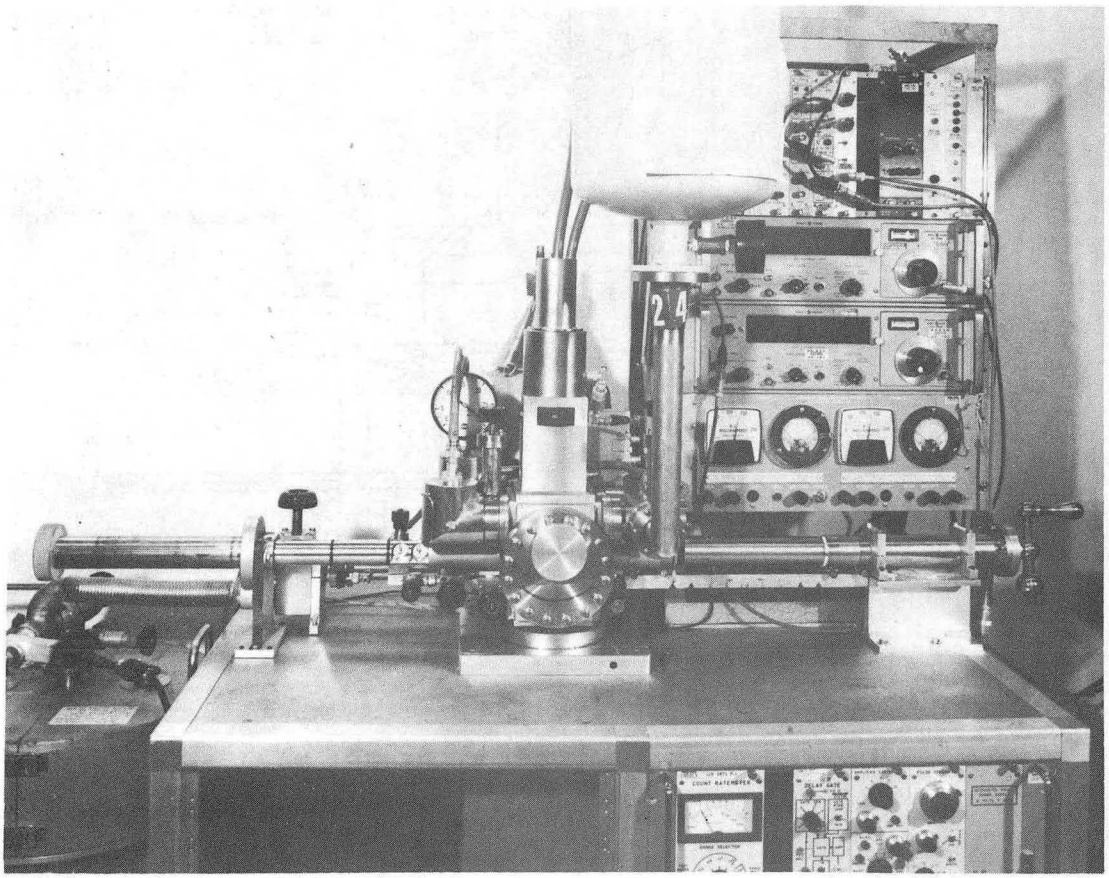

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Fig. 2

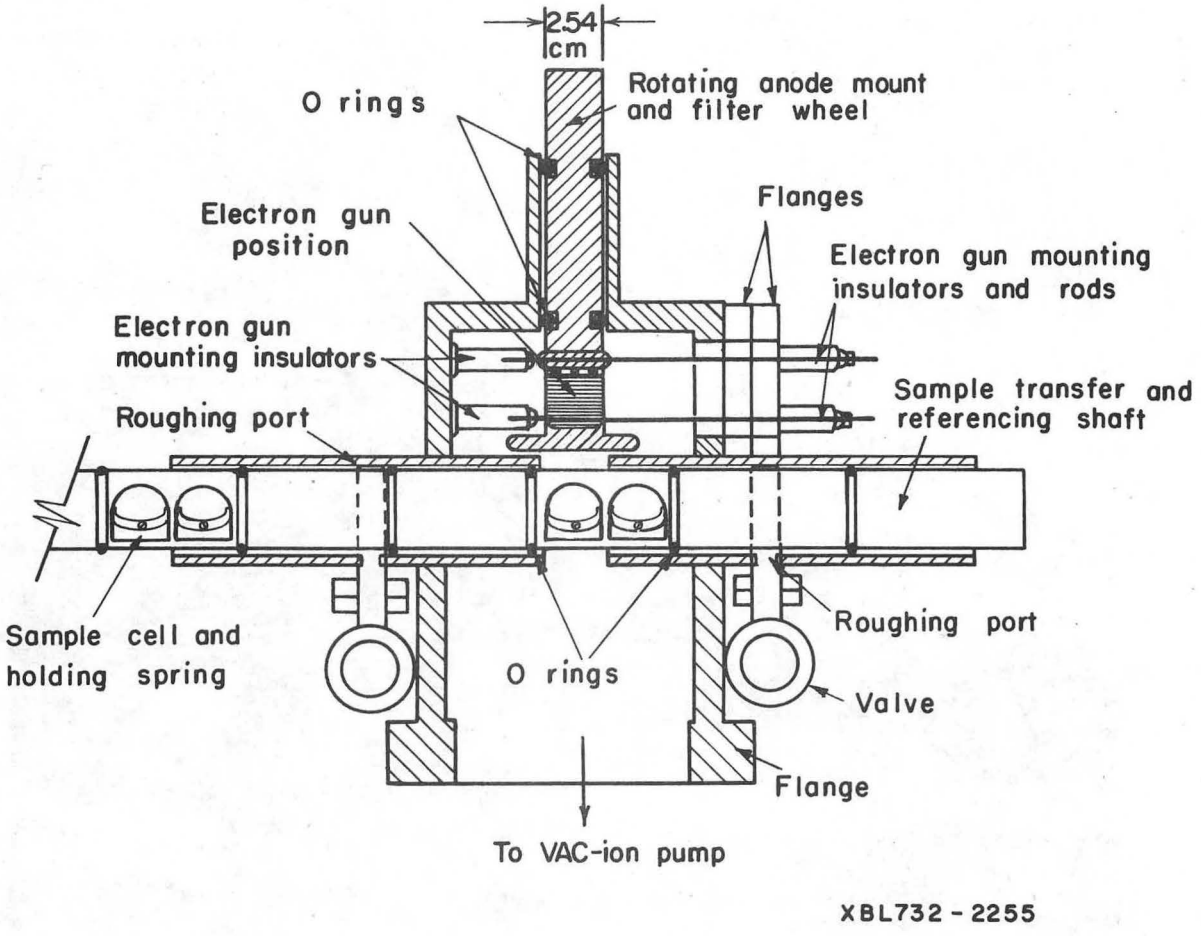
2.54 cm
O rings
Rotating anode mount and filter wheel
Flanges
Electron gun position
Electron gun mounting insulators and rods
Electron gun mounting insulators
Sample transfer and referencing shaft
Roughing port
Roughing port
Sample cell and holding spring
O rings
Valve
Flange
To VAC-ion pump
XBL732-2255

Fig. 3

0 0 0 0 4 3 0 7 1 4 5

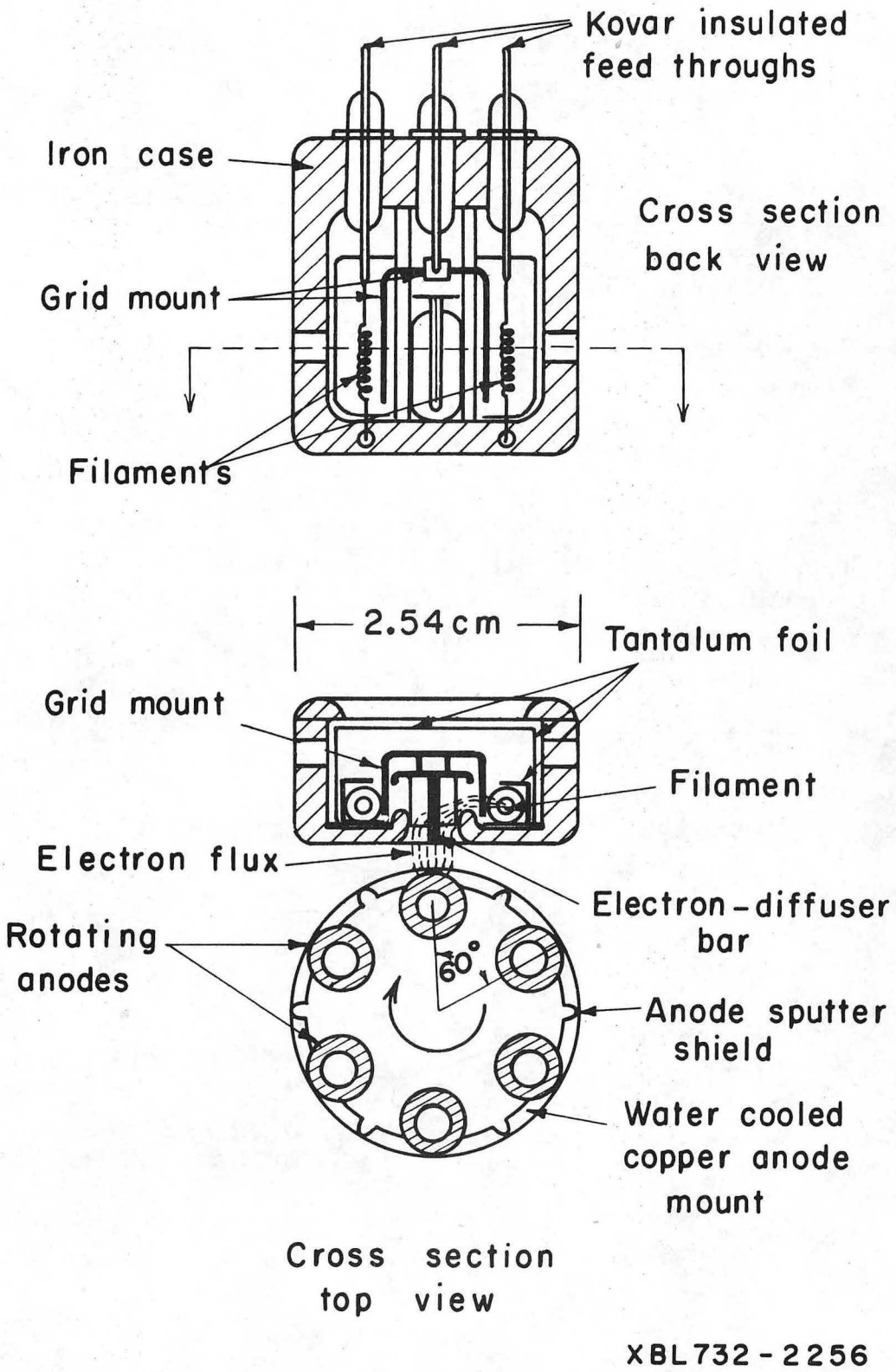

Fig. 4

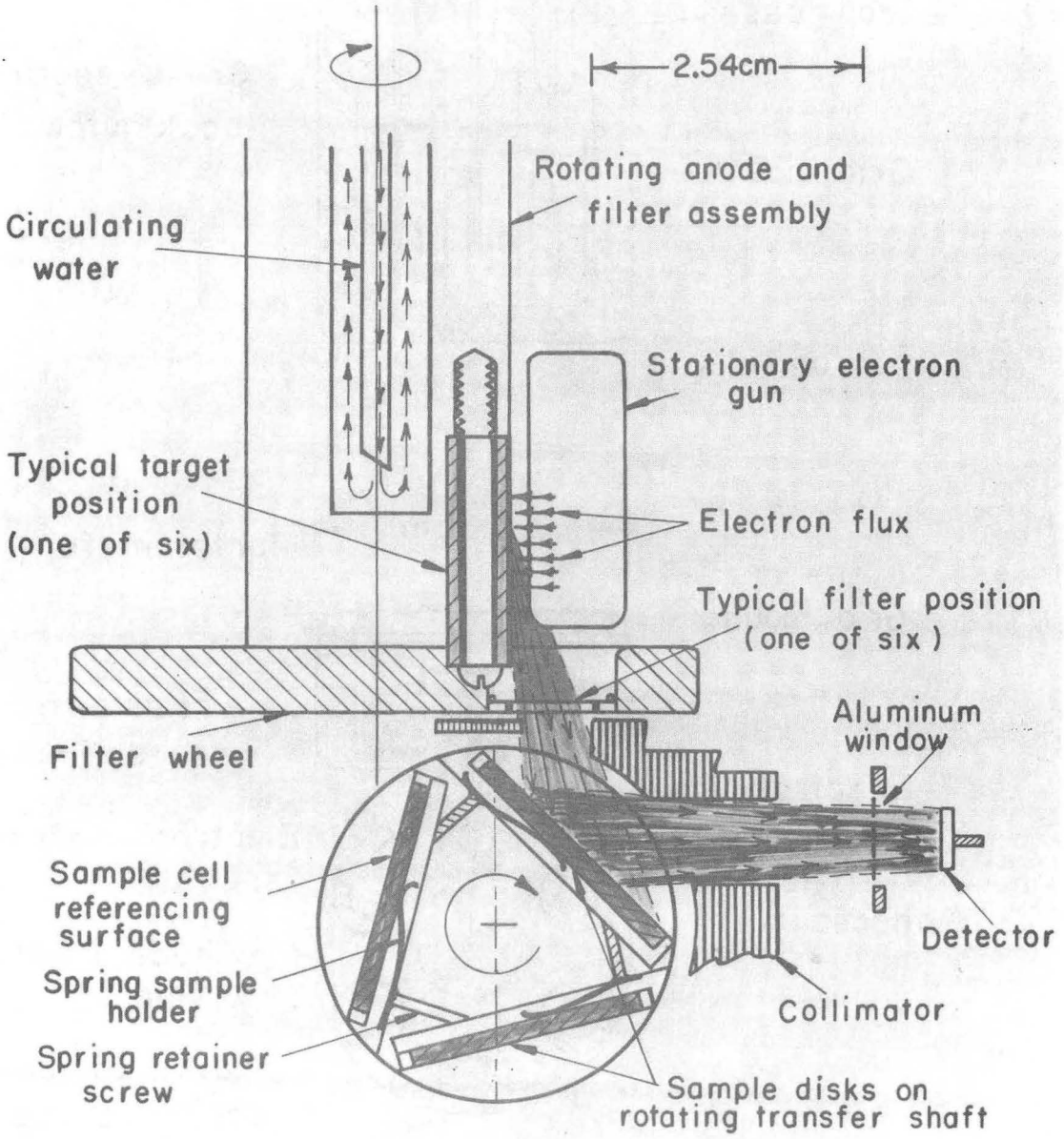

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Fig. 5

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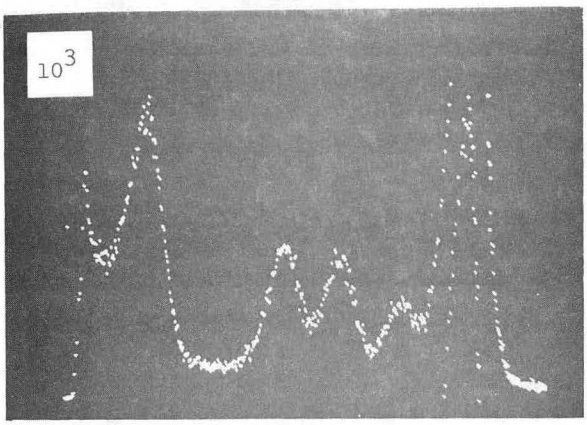
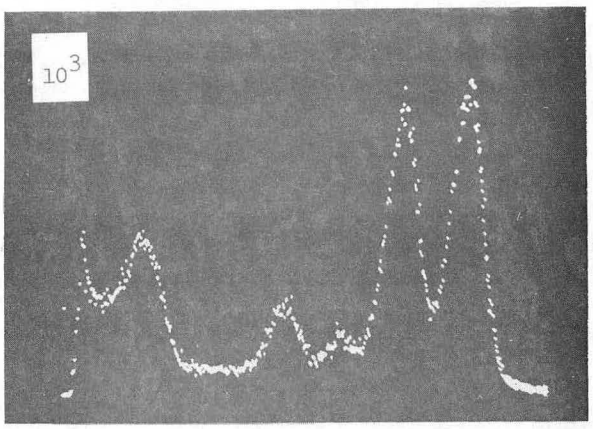


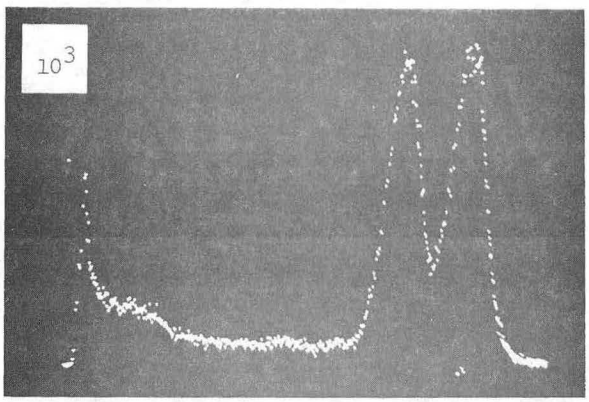
O(523eV) Na Mg Al Si 2keV

Magnesium Anode 10 min.



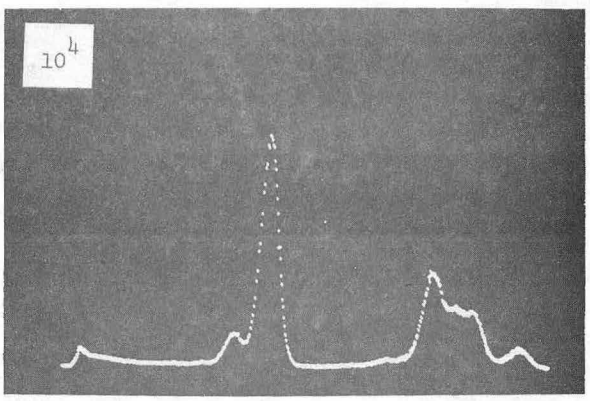
O Na Mg Al Si 2keV

Aluminum Anode 10 min.



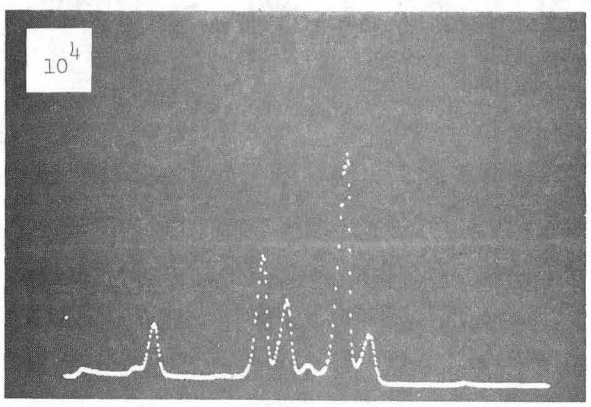
Al Si 2keV

Silicon Anode 4 min.



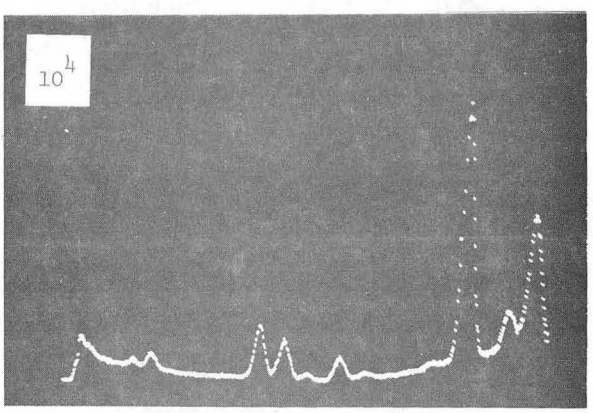
Si Ag 4keV

Silver Anode 2 min.



AlSi K Ca Ti 8keV

Titanium Anode 2 min.



AlSi K Ca Ti Mn Fe Ni 8keV

Nickel Anode 2 min.

XBB 735-3031

Fig. 6

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