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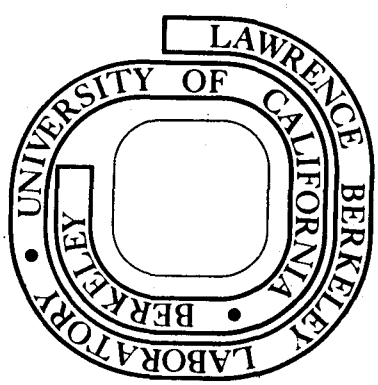

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DISCLAIMER

NON-DISPERSIVE SOFT X-RAY FLUORESCENCE ANALYSES OF ROCKS AND WATERS

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Abstract

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A six anode soft X-ray fluorescence spectrometer is used to analyze the chemistry of rocks and waters. Analyses are checked against neutron activation results for sodium and chlorine on the same samples. Preliminary experiments indicate the possibility of 5% or better results when using an appropriate accurately constructed calibration solution. The present sample size for water is 50 ul. The water sample results support the empirical geothermometer of Fournier and Truesdell, and the quartz geothermometer for $T > 125^{\circ}C$.

Hot-spring, cold spring and rock samples have been collected from four geothermal areas in North-Central Nevada. The samples have been analyzed in order to compare three chemical geothermometers, and to find if additional chemical correlations could be established to determine which geothermal area might have the best resource potential.

Analyses are performed with a previously described non-dispersive multiple anode spectrometer (Hebert, 1974). A schematic diagram of the spectrometer is shown in Figure 1. Six anodes with filters may be rotated into place sequentially without disturbing the vacuum. An important feature of this arrangement is the amount of power the sample must absorb, which in this case is estimated to be of the order of a milliwatt per square cm. This low level allows the non-destructive analysis of plastics and other samples which might be considered volatile in more energetic dispersive spectrometers.

Rock samples are collected in kilogram quantities and crushed in an ore crusher fitted with soft iron jaws. They are

then split to approximately 100 g samples and crushed with an alumina jaw crusher and fed through an alumina disk grinder for reduction to particle sizes of 100 microns or less.

A small weighed portion of the final grind is then mixed with a weighed portion of $LiBO_2$ in a 1:10 sample to $LiBO_2$ weight ratio. The mixture is fused, stirred and poured into a ring resting on a vitreous carbon surface. The molten glass is pressed with a flat gold foil inlaid in a copper block using the apparatus shown in Figure 2. The resultant ringed glass pills are then analyzed. The results for the major elements present above the one percent level are good to from one to four percent for a 2 minute analysis time per element.

Water samples are collected with a portable plastic and teflon filter unit which features a small hand operated vacuum pump. The non-metallic construction reduces contamination which might interfere in neutron activation analyses on the same samples. A filter pore size of 0.45 u is used. Wide mouth 500 ml "Nalgene" bottles are used as containers.

For X-ray fluorescence analyses of water samples, a 50 µl portion of unknown solution or standard calibration solution is pipetted onto the center of an 0.02 cm thick Lexan disk. (Lexan is an aromatic polycarbonate plastic.) Each disk has a 9 mm diameter circular scratch handscribed on center on the back side. When a disk is placed on a leveled hot plate surface for evaporation at 50° C with the circular scratch down, it takes on the shape of a slightly dished flat-bottomed saucer. A pipette rinse and sample fixing solution containing 1.20 g spectroscopic grade $LiBO_2$ plus 1.00 g acetic acid per liter is taken up and added to the sample droplet. The sample fixing solution has two drops (approximately 80 mg) of water soluble glue (Elmers Glue All) per 50 ml added just prior to use. The samples may be fixed on disks in the field or at the laboratory. The portable field evaporation unit is shown in Figure 3.

The resulting spots on the Lexan disks have an area of 0.7 cm^2 and a thickness of 2 to 5 u. Several prepared samples along with some blank disks are shown in Figure 4. A list of the elements analyzed and the sensitivity (3 standard deviations) for a 2 minute analysis time for each element is given in Table I.

X-ray absorption corrections for thin water residues are made by assuming homogeneity and applying a method similar to that described by Norrish and Chappell (Norrish, 1968) in an iterative manner. The X-ray absorption coefficients of McMaster et al (McMaster, 1969) are used.

The reproducibility observed for 45 analyses on 19 different samples was better than 5% for chlorine and 12.7% for sodium at concentrations ranging down to 10 and 20 ppm respectively. Comparisons with neutron activation results for these elements indicate agreement within the expected uncertainties for most samples.

In order to test for the possibility of water contamination by leaching of container walls, or of a change in water composition due to plating out of any components, the walls and bottoms of several polyethylene and Nalgene containers were analyzed directly. Samples were prepared by cutting and carefully making disks of the container walls.

The X-ray spectra observed are shown in Figure 5 and Figure 6 along with a typical water standard and a Lexan blank. Spectra (a) and (b) in Figure 5 are of a polyethylene container that held hot spring water for over one year and an empty identical type container. The magnesium (Mg) peak in the Figures is due to the exciting radiation and the large lump to the right is due to scattered bremsstrahlung. Spectra (5c) and (5d) show the same situation from the insides of "Nalgene" bottles. The increased signals in (5c) corresponds to roughly $\frac{1}{4}$ drop of hot spring water residue which probably remained after emptying the bottle for testing. Figure (6a) and (6b) show a similar situation for "Nalgene" where less residue is apparent. Some variability in Nalgene lot compositions is suggested by a comparison of the bottle spectrum in Figure (5d) and those shown in (6a) and (6b).

Figure (6c) and (6d) illustrate a typical magnesium anode run on a water sample calibration solution and a blank run for a Lexan disk plus distilled water and fixing solution. Our silicon analyses would be improved if a roll of Lexan could be

found with less silicon in it. The magnesium anode is used for sodium analyses only. The peaks seen at higher energies are bremsstrahlung excited.

Figure 7 illustrates a comparison between the quartz geothermometer and the sodium-potassium geothermometer. The agreement is poor. Figure 8 shows the results for the sodium-potassium-calcium geothermometer of Fournier and Truesdell (Fournier, 1972) as compared to the quartz geothermometer. The upper points labeled 8 should be B for Bradys. They are in good agreement with the maximum measured down hole temperature observed at the time of drilling (212° C). The points labeled 10 are also in agreement with the maximum down hole temperature of a series of wells drilled 150 miles to the east at Beowawe and measured at 214° C at that time.

It appears that while there may be some problems at low temperatures, the higher temperature results for several hot spring sites are in general agreement and may be representative of the temperatures at depth of hot spring reservoirs.

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REFERENCES

Fournier, R.O., and Truesdell, A.H., 1972, An empirical Na-K-Ca geothermometer for natural waters, Geochimica et Cosmochimica Acta, v 37, p. 1255.

Hebert, A.J., and Street, Kenneth Jr., 1974, Non dispersive soft X-ray fluorescence spectrometer for quantitative analysis of the major elements in rocks and minerals, Analytical Chemistry, v 46, p. 203.

McMaster, W.H., Kerr Del Grande, N., Mallett, J. H., and Hubbell, J.H., 1969, Compilation of X-ray cross sections, UCRL 50174, Sec. II, 350pp., distributed by National Technical Information Service, U.S. Dept. of Commerce, 5285 Port Royal Road, Springfield, Va 22151.

Norrish, K., and Chappell, B.W., Physical Methods in Determinative Mineralogy, J. Zussman, Editor, p. 196, Academic Press, New York, 1967.

Table I. Elements analyzed and the observed sensitivity (3 standard deviations) for typical 2 minute per element analyses.

Element	Sensitivity (ppm)
Na	5
Mg	3
Al	5
Si (SiO_2)	10
P	8
S ($S^=$, S^o, $SO_4^=$)	8
Cl	4
K	2
Ca	2
Ti	2
Cr	2

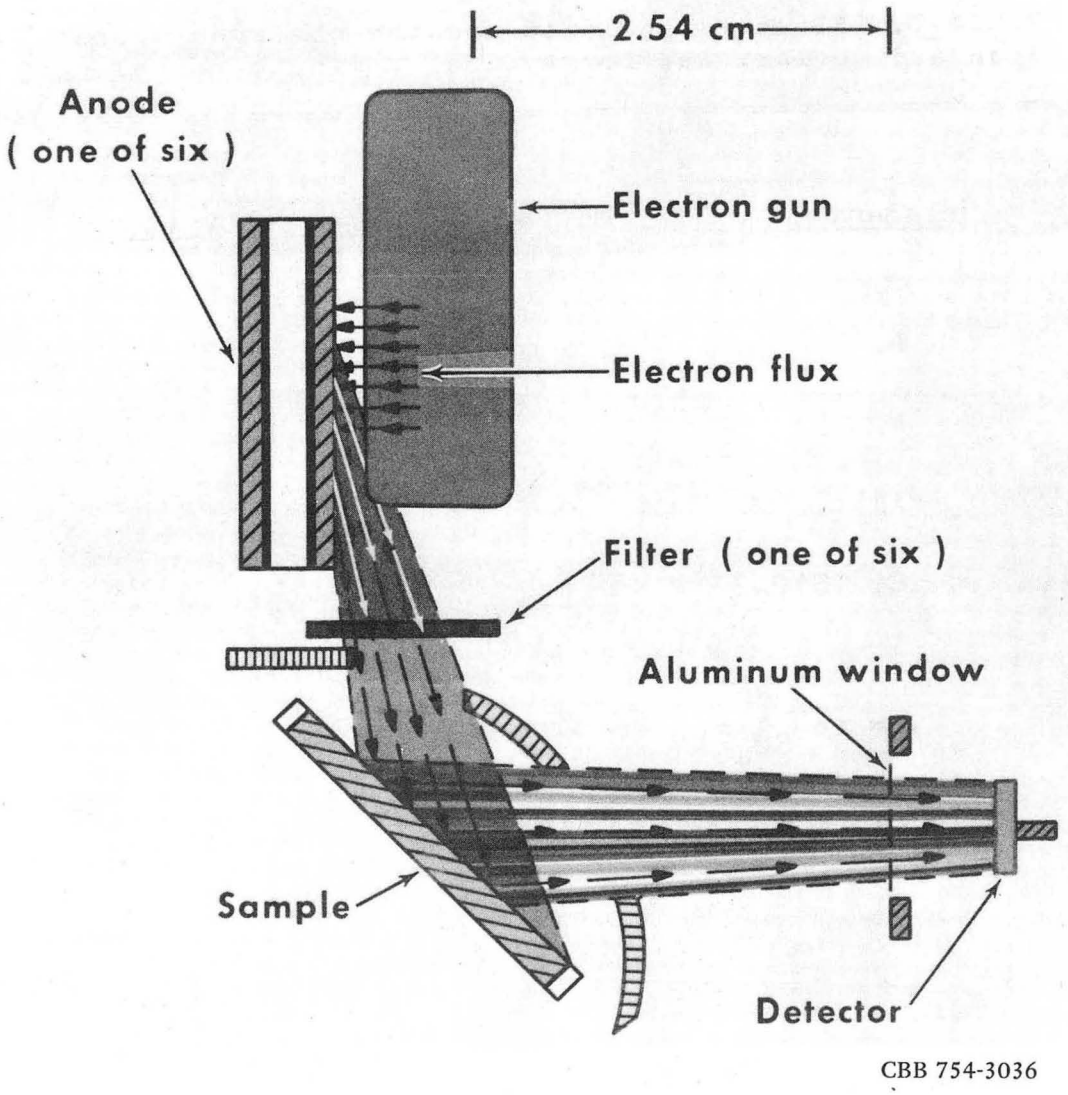

Figure 1. A schematic diagram of the non-dispersive soft X-ray fluorescence spectrometer.

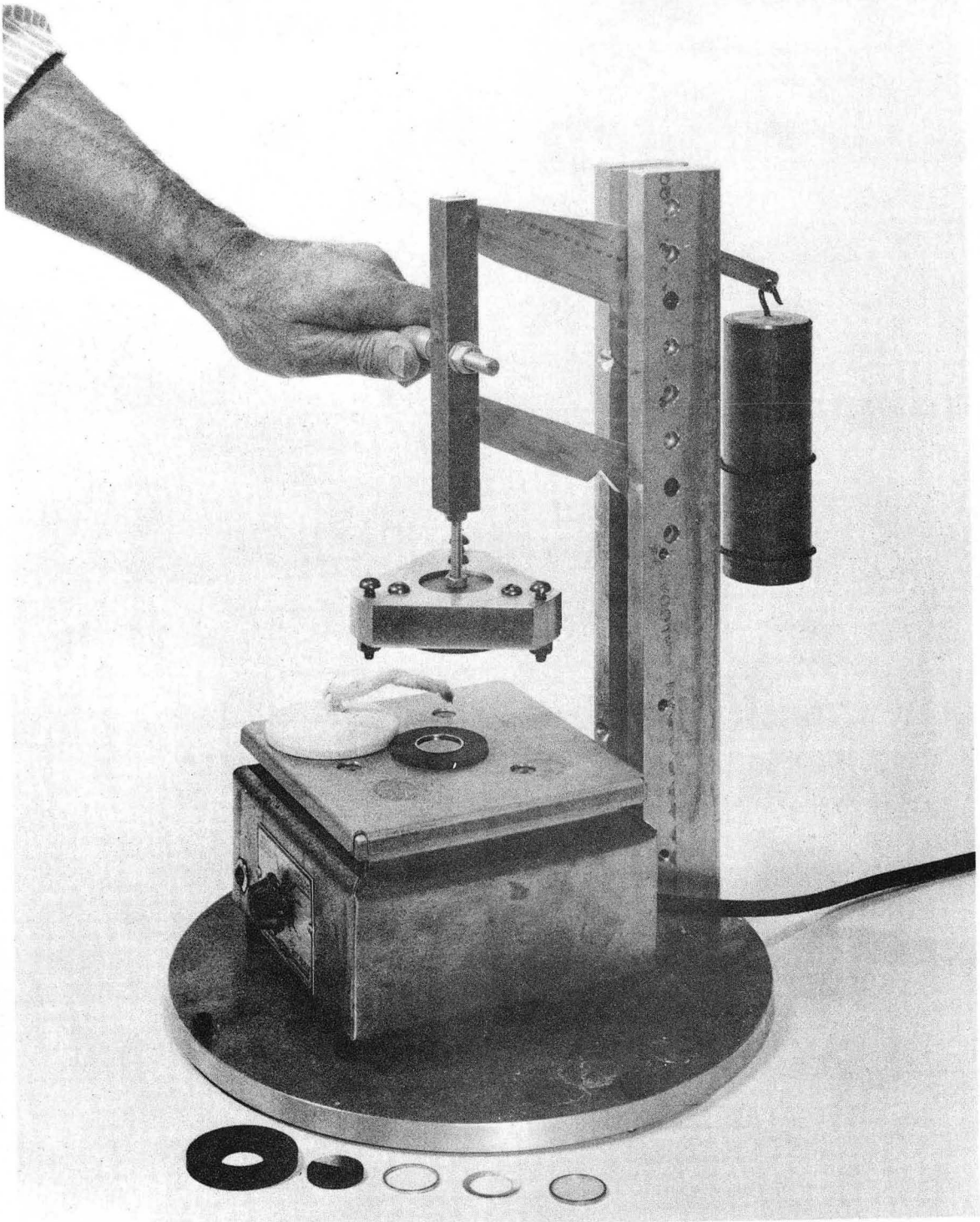

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Figure 2. Molten glass sample press.

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Figure 3. Portable heater and field evaporation unit.

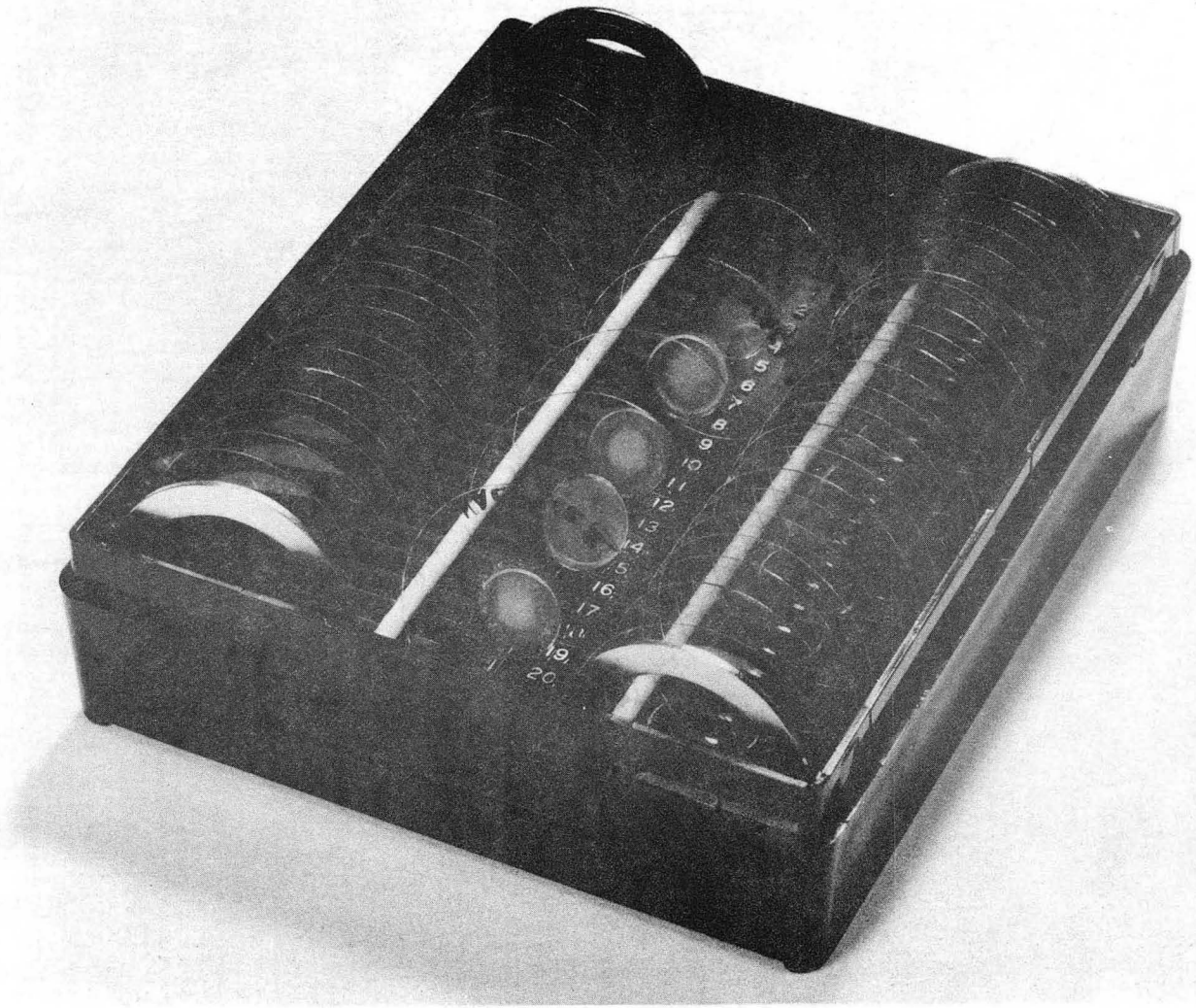

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Figure 4. Evaporated water and fixing solution spots on Lexan disks along with some blank disks.

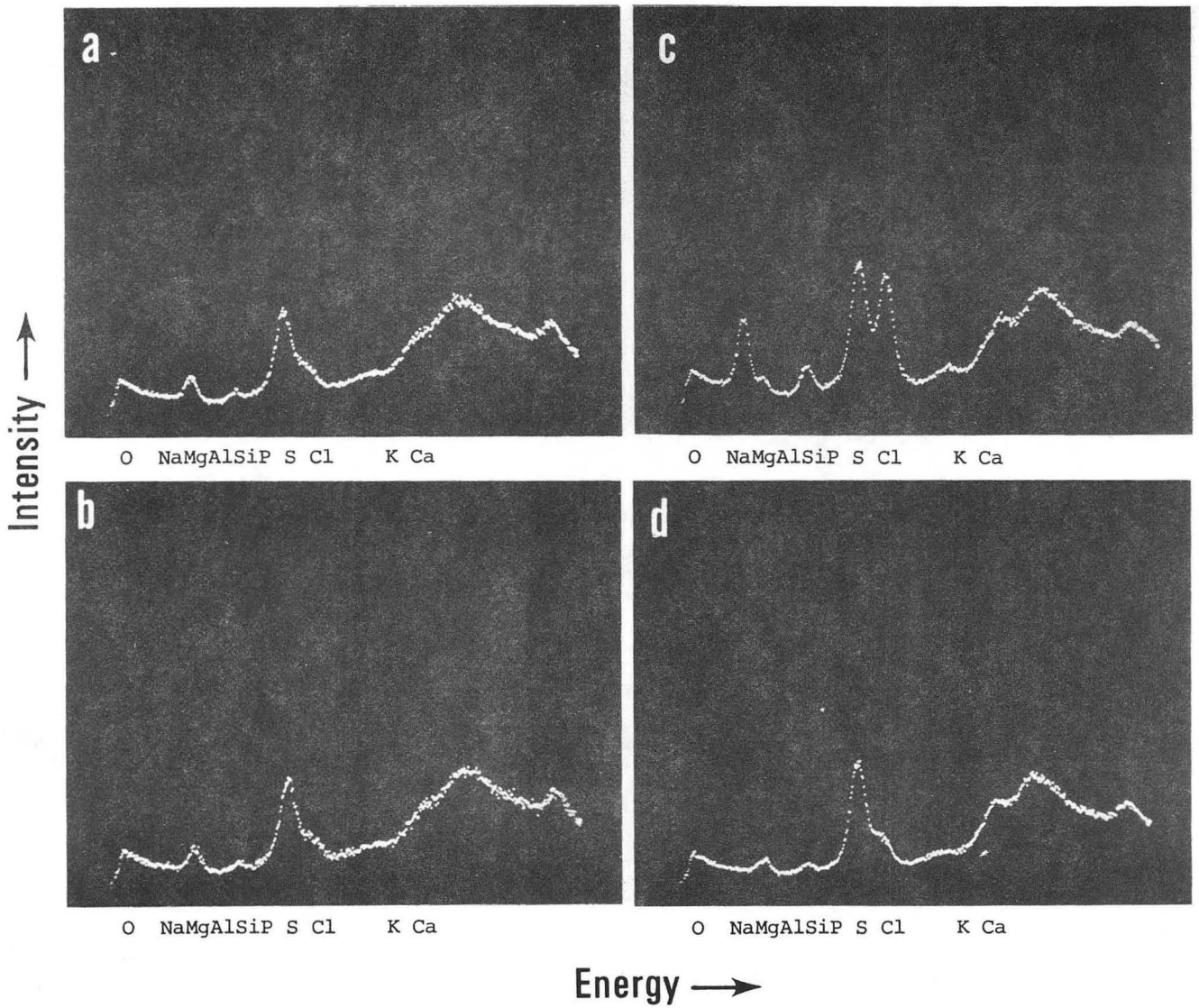

Figure 5. Observed spectra for plastic sample container walls. Intensity full scale is 5×10^4 counts per channel, and the highest X-ray energy is 7 keV.

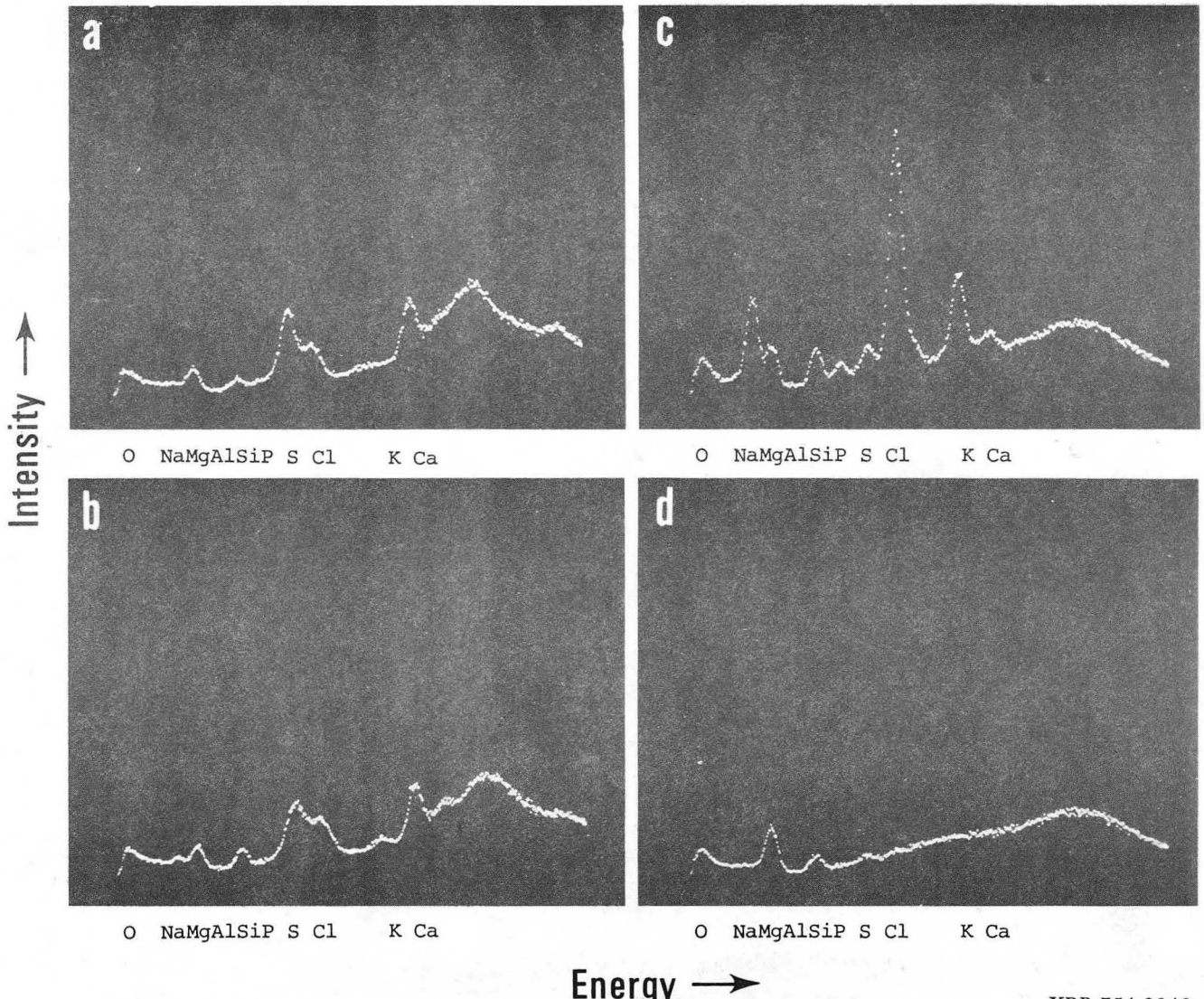

Figure 6. Observed spectra for Nalgene container walls are shown in (a) and (b), while those shown in (c) and (d) are of the calibration solution and a blank. Intensity full scale is 5×10^4 counts per channel and the highest X-ray energy is 7 keV.

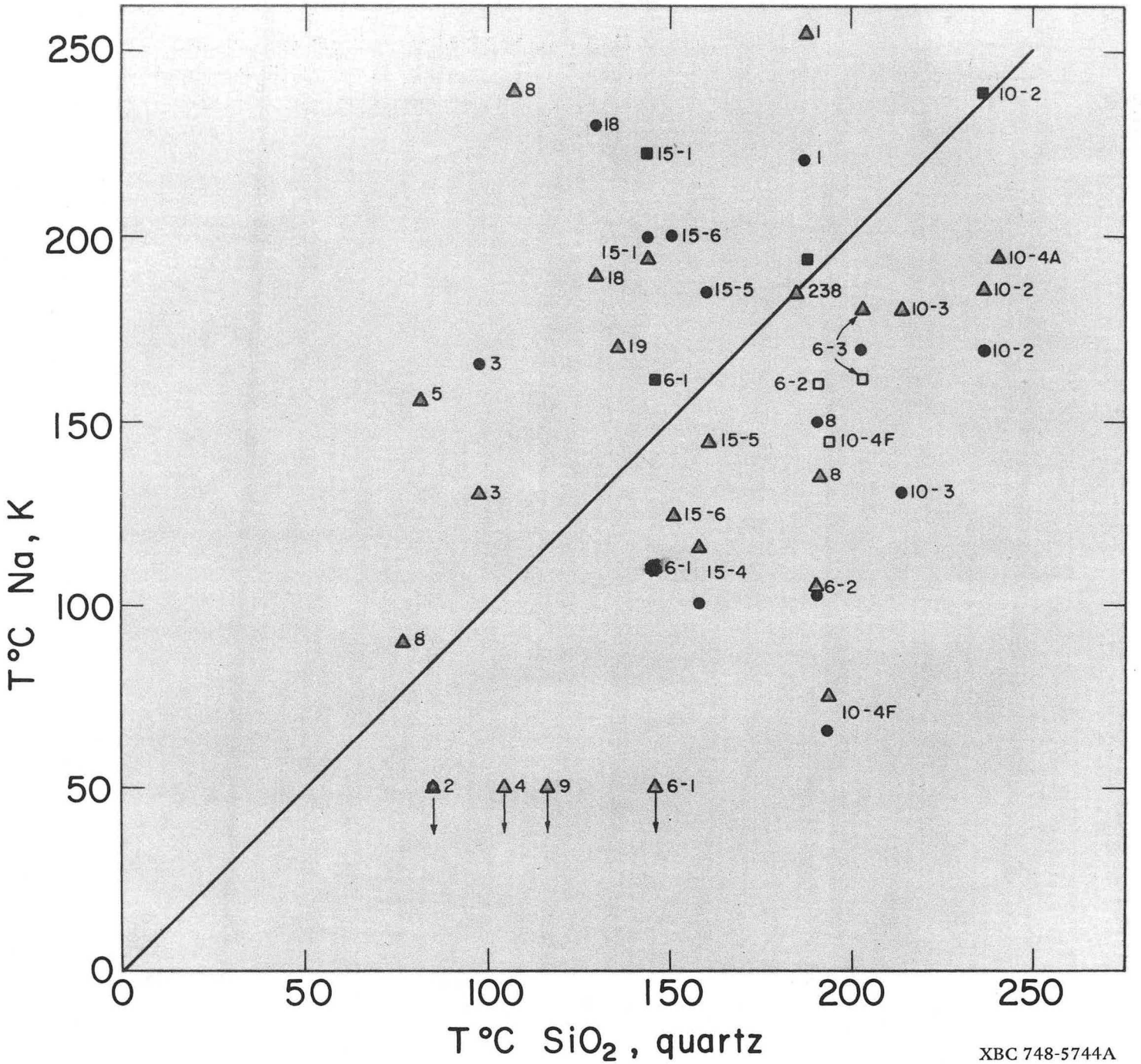

Figure 7. Sodium-potassium geothermometer results plotted versus those for the quartz geothermometer.

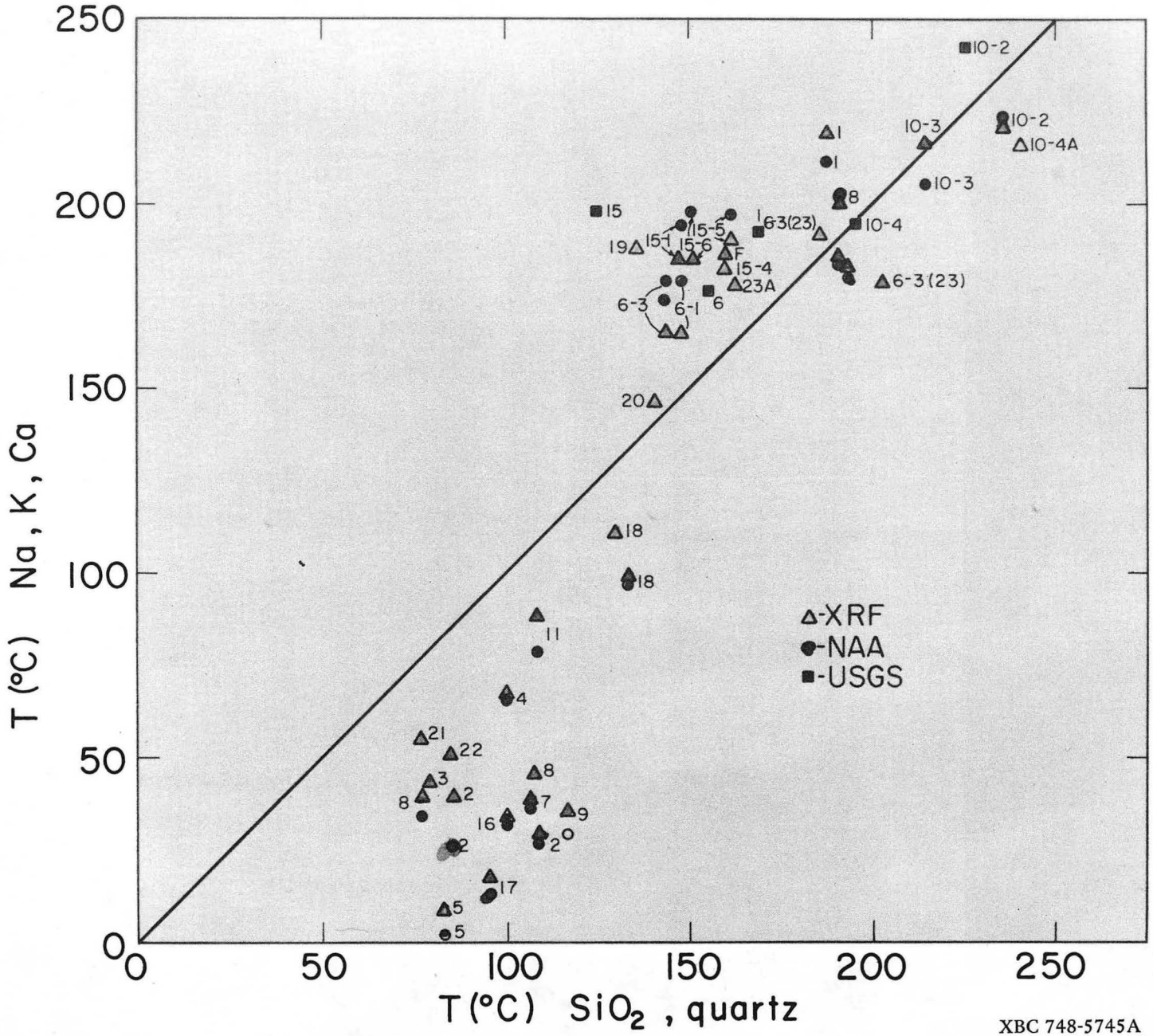

Figure 8. Sodium-potassium-calcium geothermometer results plotted versus those for the quartz geothermometer.

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