SEARCHING FOR VOLATILE SUPERHEAVY ELEMENTS

S. Yashita and R. E. Leber

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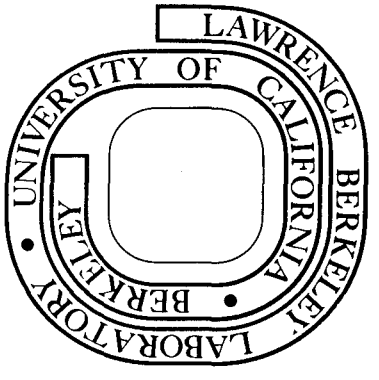

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SEARCHING FOR VOLATILE SUPERHEAVY ELEMENTS

S. Yashita and R. E. Leber

Lawrence Berkeley Laboratory
University of California
Berkeley, California

ABSTRACT

Developed as part of the experimental search for superheavy elements (SHE), the system described here has been used for the analysis of gaseous radioactivities with half lives greater than thirty minutes. Collected with high efficiency on a surface cooled to liquid-nitrogen temperature, alpha and fission activities are counted with solid-state and dielectric detectors. Procedural details and experimental observations are presented.

INTRODUCTION

There have been predictions (1-3) that through enhanced binding of valence electrons some of the superheavy elements (for example, 112, 114, and 118) may be chemically inert and volatile. Considerations of the finite size of the nucleus, the orbital velocities and the angular momenta of electrons in these high-Z atoms indicate that relativistic and spin-orbit effects may significantly influence electron energy and spatial distributions, thereby potentially modifying chemical behavior.

Splitting of the p, d, and f shells into subshells: $j = \ell + 1/2$ and $j = \ell - 1/2$ may stabilize, say, elements 112 and 114 to the extent that their respective $7s^2$ and $7p_{1/2}^2$ configurations will represent shell closures. Thus, both the binding and promotion energies of the valence electrons in these elements would be increased. Radial contraction (4) of low-momentum ($\ell - 1/2$) electrons due to relativistic terms could change the degree of screening of the nuclear charge as well as the "softness" and angular distribution of the electron cloud and thus alter the chemistry of these elements. Evidence in support of predictions of an increase in chemical inertness and volatility of the superheavy elements over their lighter homologs may be obtained by extrapolating (2) the properties of known elements *.

The trend in boiling points for the IIB elements is shown (open circles) in figure 1. Linear extension of these data indicate

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* We consider here elements of the IIB group because their electronic structure limits the uncertainties in oxidation states.

that the boiling point of element 112 approaches room temperature. Furthermore, extrapolation (3) of the standard enthalpy for the monatomic gas gives element 112 the low value of 5.3 ± 1.0 kcal/mole.

In addition to the systematics of volatility, parameterized chemical inertness is presented (triangles) in figure 1. Approximated by the sum of the first two ionization potentials (assuming divalent species) weighted by r_2^+, the ionic radius, (to compensate for differential screening effects), the inertness is shown to increase with heavier elements. This reduced chemical reactivity is also indicated in figure 2 by the heat-of-formation curves for the aqueous halides. Independent work reported in Refs. 1, 5, and 6 finds that, of the dihalides, only the fluorides are likely to be stable. It is proposed (1) that the free energies of formation of the element-112 salts will exceed by 70 kcal/mole those of the corresponding mercury compounds. Accordingly, only the formation of $(E112)F_2$ will proceed exothermically. (The anionic halide complexes $MCl_4^{-2,-3}$ and $MBr_4^{-2,-3}$ are predicted to be stable, however.) Empirical data clearly show the increasing endothermicity of reactions with the heavier IIB elements.

Hence, unless element 112 (eka-mercury) were to be stabilized as the fluoride or through hybrid bonding strong enough to offset spin-orbit splitting (7), we would expect it to be relatively inert and volatile. Moreover--depending on the number and binding energy of their valence electrons--other superheavy elements may show similar behavior. Elements with these properties could readily

escape from conventional chemistry, so a system to trap and analyze evolved radionuclides has been designed.

The gas-analysis technique described here is based on charcoal adsorption-desorption with subsequent condensation and counting. It is sensitive to sub-nanobarn yields of a gaseous superheavy element whose half life exceeds about thirty minutes.

EXPERIMENTAL APPARATUS AND METHODS

Figure 3 is a line drawing of the gas-handling system (analogous to that mentioned in Ref. 8) used in these studies. The activity is trapped in and desorbed from charcoal located in the glass U-tube. During the adsorption phase of an experiment, the tube is placed in a small plastic bag to protect it and its external heating tape from the cooling medium (here, a water-ice/NaCl bath). Desorption of the activity is accomplished through resistance heating. The temperature of the charcoal trap is continuously monitored with a Chromel/Alumel thermocouple.

^{222}Rn ($T_{1/2}$ = 3.8 days) is used to calibrate and measure the efficiency of this apparatus. The temperature dependence of radon release from the charcoal has been measured and is included as figure 4. From this desorption curve and knowledge of the heats of adsorption of rare gases (Table 1), we can estimate temperatures for the desorption of super-heavy elements.

Table 1: Isosteric Heats of Adsorption on Graphitized Carbon at Zero Coverage (9)

Gas	q (cal/mole)
Neon	849
Argon	2355
Krypton	2999
Xenon	4059

After being released from the charcoal, gases migrate (by cryogenic pumping) to a surface cooled to liquid-nitrogen temperature (-195 °C.). In the course of our experimentation we have condensed the volatiles directly on the (cross-sectional) surface of the copper rod immersed in the coolant and on a mica disk which had been clamped to the rod with Dow Corning Heat Sink Compound used to provide thermal continuity. We achieve quantitative condensation at the top surface of the copper rod by using a Teflon collar to restrict gas access to the sides of the rod. The condensation efficiency has been found to be 94 ± 4% on the copper surface and 90 ± 8% on the mica*. Positioned 2.5 mm from the condensate, the solid-state detector has nearly 2π geometry. The total counting efficiency for this system is 7 ± 1%, determined by calibration against a detector assembly of known efficiency.

The electronic circuitry used in this work is shown in the block diagram figure 5. Prior to its registration in multichannel analyzers and scalers, an event is subject to pile-up and noise rejection. A state-of-the-art pile-up rejecter is used to resolve high-energy events from stacked-up alpha pulses. The resolving time for this counting system with pile-up rejection has been found to be 95 ± 15 ns (versus 500 ± 50 ns without pile-up rejection). In addition to reducing the number of high-energy artifacts in a spectrum, this mode of operation improves resolution by greatly reducing low-energy peak tailing. The noise rejection network eliminates the accidental counting of local transients. Delay modules are used in adjusting signal timing to

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* The condensation efficiency of the mica shows a strong dependence on the uniformity of the compound film at the mica-cooling rod interface and on the thickness of the mica sheet.

insure that an event satisfies the necessary anti-coincidence conditions.

The targets used in this work are primarily 10-mil (0.025-cm) uranium collimators which have been treated with 6M HNO_3 to remove the oxide surface layers. After heavy-ion irradiation, the target is placed in a side-arm flask which is connected with Tygon tubing to a helium cylinder and--via a calcium sulfate drying tube--to the cold (-20 ^{o}C.) charcoal trap. (New cocoanut charcoal which has been baked out under vacuum for several hours is used in each run.) After purging the apparatus of air for a minute and adjusting the helium flow rate to ~1 ml/s, the target is dissoved in 5 ml of 9M HCl introduced with a syringe. (It has been determined that volatiles are removed here from non-volatiles and aerosols with a separation factor greater than 10^7.) To allow complete transfer of gases to the charcoal the helium flow continues for five minutes at which time the trap is closed off and connected to the vacuum system.

Desorption is effected by gradually heating the charcoal to about 325 ^{o}C. and allowing the gaseous products to escape into the evacuated ($\lesssim$ 10 mTorr) manifold. Condensation and counting of the activity then proceed as indicated above. The overall procedure takes a minimum of 15 minutes from the end of the bombardment.

RESULTS AND DISCUSSION

While we cannot establish the production of superheavy elements from these experiments, we did observe a good yield of volatile alpha activity which we have assigned to radon isotopes. Produced in the bombardments of natural uranium with ^{40}Ar, ^{48}Ca, ^{86}Kr, and ^{136}Xe (see Table 2), radon isotopes 207 through 212 inclusive were identified by the alpha decay and half-lives of their respective astatine electron-capture daughters. The 0.7 ± 0.2 mb production cross section of ^{211}Rn estimated for reactions of ^{nat}U with full-energy (8.5 MeV/A) ^{136}Xe is consistent with mass yields found by Otto, et al (10). These nuclides result from the exchange of nuclear material between target and projectile nuclei in quasi-fission or deep-inelastic scattering. Moretto and Sventek (11) have developed a model which describes the reaction-product yield distribution in terms of diffusion within an intermediate complex. The degree of equilibration and the lifetime of the complex determine the nuclei produced.

Our experiments give some evidence for the existence of a 7.8 MeV alpha activity which decays with a half-life of less than 30 minutes. There has been considerable difficulty in acquiring sufficient data on this decay, however, since the time spent on chemistry and gas handling precludes resolution of the shorter half-lives. If the observed 7.8 MeV alphas are due to a discrete radioactivity, they may be attributed to the electron-capture decay of a state in ^{212}Rn to ^{212}At. The branching in this case would be approximately 0.5%, in keeping with the $\lesssim 1\%$ limit reported by Momyer, et al (12).

Table 2 indicates the results and SHE detection limits for these experiments. Three high-energy events have been observed in two separate ^{136}Xe bombardments. The energies for these events are 110, 68, and 40 MeV and they were detected respectively 1, 18, and 24 hours after the end of bombardment. A mica detector present during the experiment which produced the 68 MeV count registered a single track. Scanning the larger piece of "control" mica from which the detector was cut revealed no tracks. Four-day background counts before each experiment showed no high-energy counts.

Table 2: Experimental Results for SHE with 30 min $\leq T_{1/2} \leq$ 100 hours

Reaction	$E^{lab}_{projectile}$ (MeV)	High-Energy Events (E > 30 MeV)	Detection Limits* (nb) σ_{SF}	σ_{α} (E > 10 MeV)
$^{40}Ar + ^{238}U$	260 - 340	0	0.5	1.0
$^{48}Ca + ^{238}U$	300 - 380	0	1.4	7.0
$^{86}Kr + ^{238}U$	560	0	7.0	15.0
$^{136}Xe + ^{238}U$	1155	3	0.4	2.0

* Much of the variation in these limits can be attributed to differences in detection geometry.

These observations cannot be unequivocally assigned either to contaminants or electrical artifacts or to produced radioactivity. If these events are not due to accidental counts, excited states in ^{212}Rn or heavy elements--possibly SHE--may be considered as explanations for the data.

Coupling of high-spin particle and hole states outside the ^{208}Pb core may yield isomers in ^{212}Rn with spins of 20 or more. Placement of these levels at about 8 MeV excitation would indicate the presence of high-energy ($\sim$15 MeV) alpha decay to ^{208}Po as well as a virtual fission barrier of only 4 or 5 MeV. In these studies, we have seen--in addition to fission events--evidence for high-energy alpha decay. Singles and γ - γ coincidence studies of high-spin nanosecond isomers of ^{212}Rn have recently been reported by Horn, et al (13) and by the Brookhaven-Chalk River-Helsinki-Stockholm collaboration (14).

Volatile superheavy elements would be produced in these experiments as deep-inelastic transfer products. If the intermediate complex in the ^{136}Xe + ^{238}U reactions becomes mass equilibrated, the derived charge-to-mass ratio (0.39) would give 302 as the most probable mass for element 118 (eka-radon). The most probable isotope would thus have N = 184, which is expected to be a magic neutron number. Attempting to produce and detect lighter isotopes of element 118, Aumann, et al (15) have bombarded ^{181}Ta and ^{170}Er with ^{136}Xe.

Further research on volatile radioactivities will contribute to our understanding of the production and decay mechanisms of radon isotopes and, perhaps, of superheavy elements. With the technique described here--in addition to decay studies--information on the phase and chemistry (through chromatographic separation from known materials) of new activities may be provided. The importance of investigating short-lived activities must be emphasized, however.

Fast separation (for example, gas-jet transport) of reaction products from background radioactivity followed by condensation of the less volatile components with subsequent spectroscopy of the gaseous fraction will significantly add to our knowledge of volatile radioactivities.

We wish to acknowledge helpful discussions with H.F. Lucas, Jr. of the Argonne National Laboratory.

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FIGURE CAPTIONS

Fig. 1: Empirical trends indicative of increasing volatility (open circles) and chemical inertness (open triangles) in the IIB elements (see text)

Fig. 2: Systematics of heat of formation for IIB aqueous halides (The unconnected dots represent the free energy of formation for aqueous chlorides.)

Fig. 3: Line drawing of gas-handling apparatus

Fig. 4: Desorption behavior (thermal release) of ^{222}Rn from activated charcoal

Fig. 5: Block diagram of counting electronics

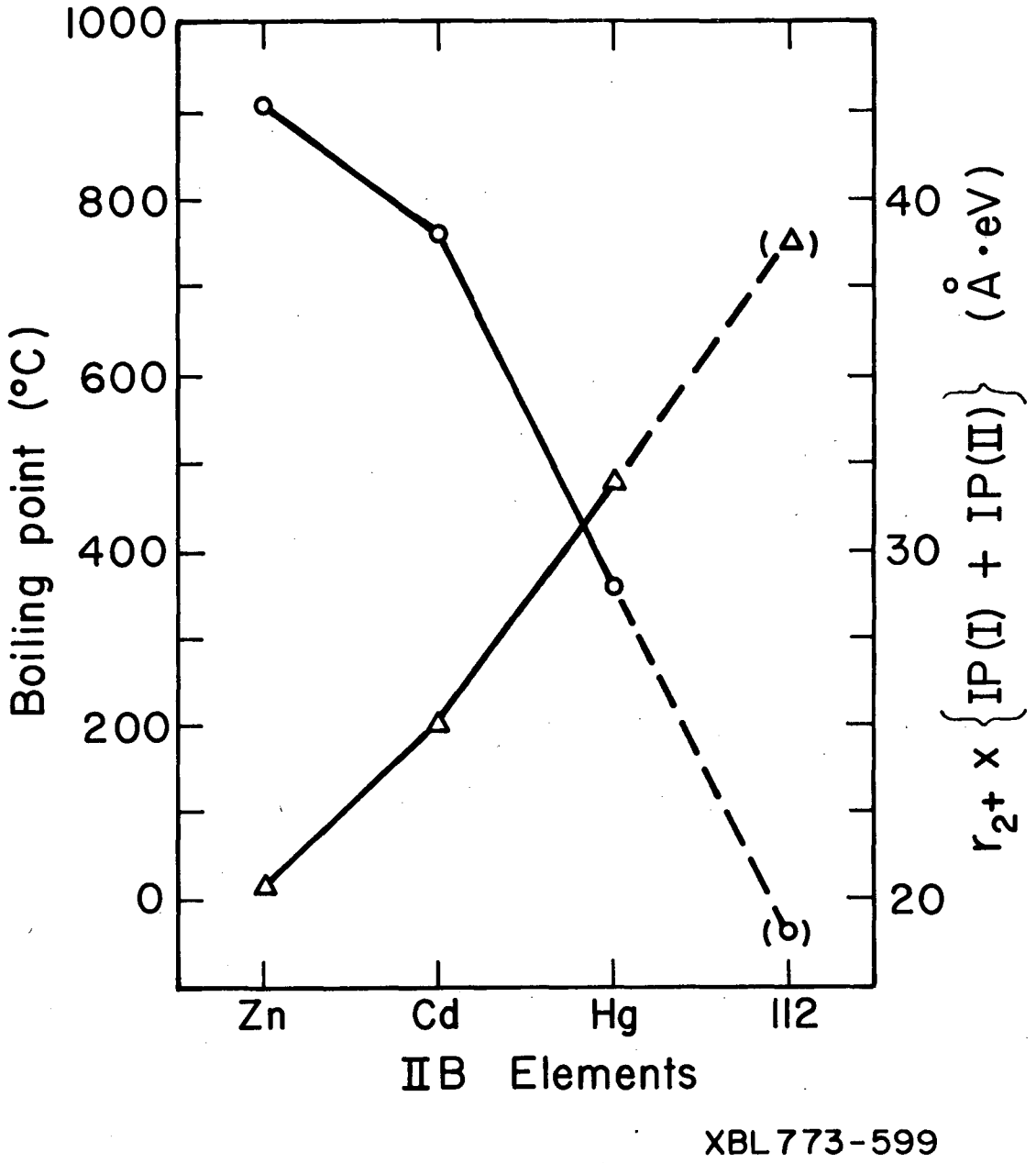

Figure 1

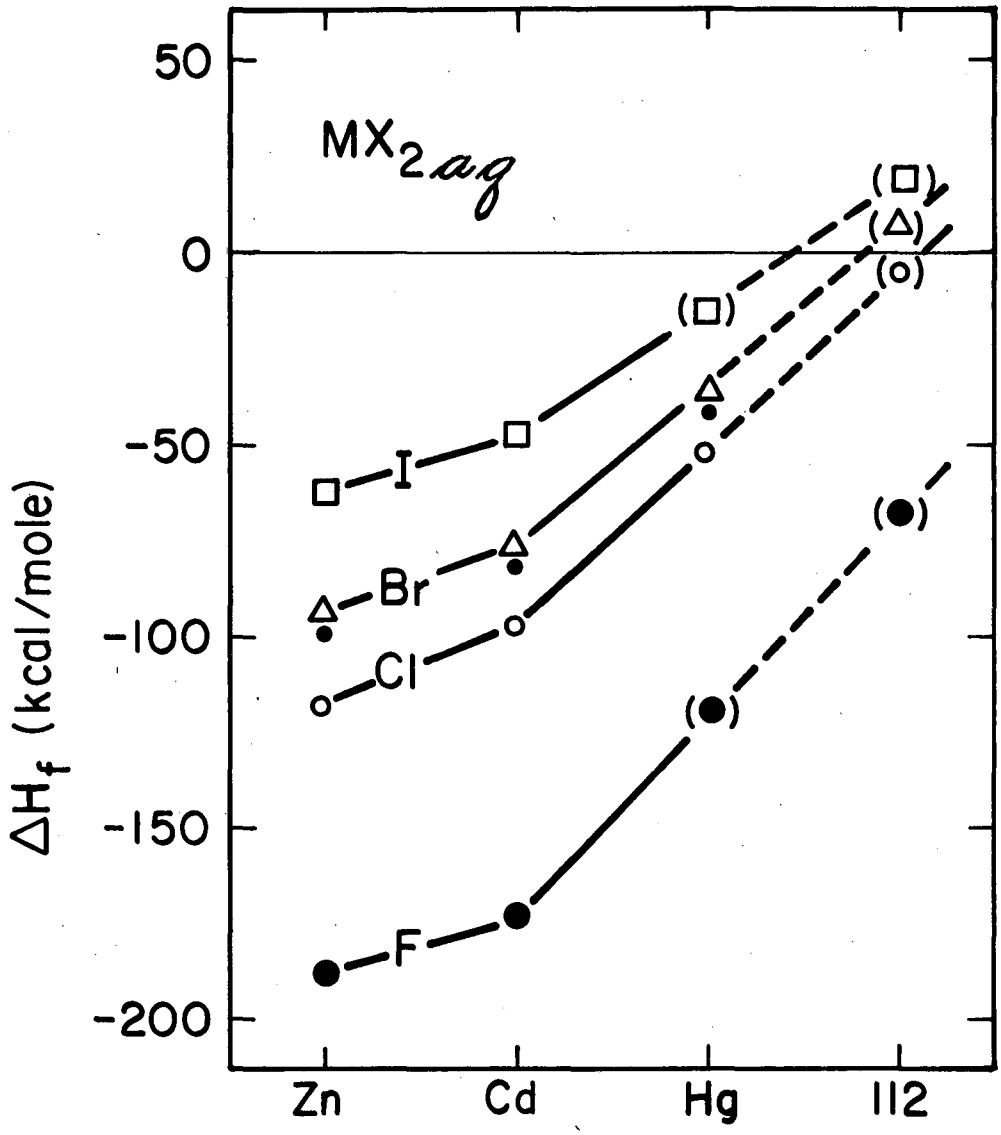

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Figure 2

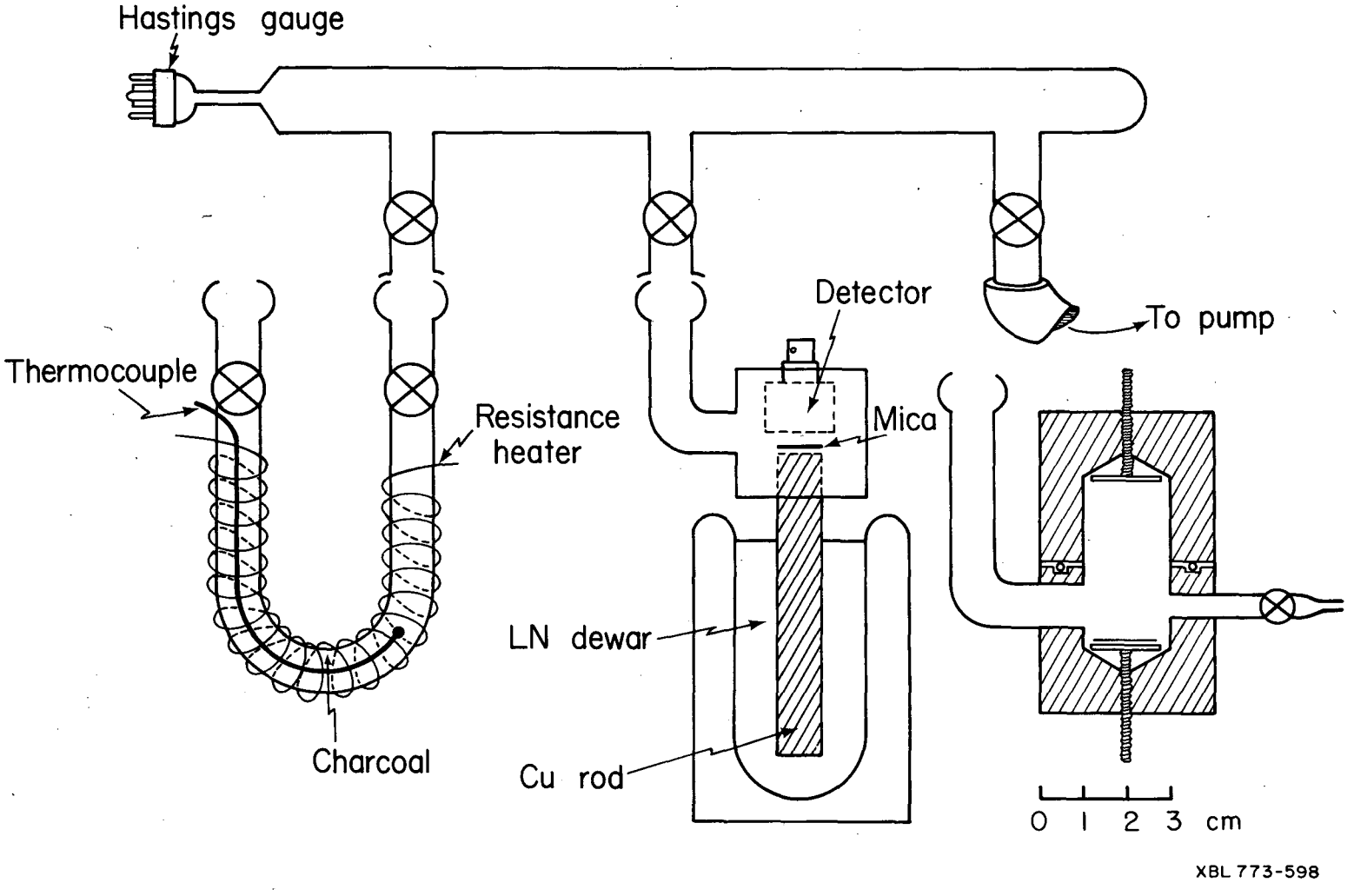

Figure 3

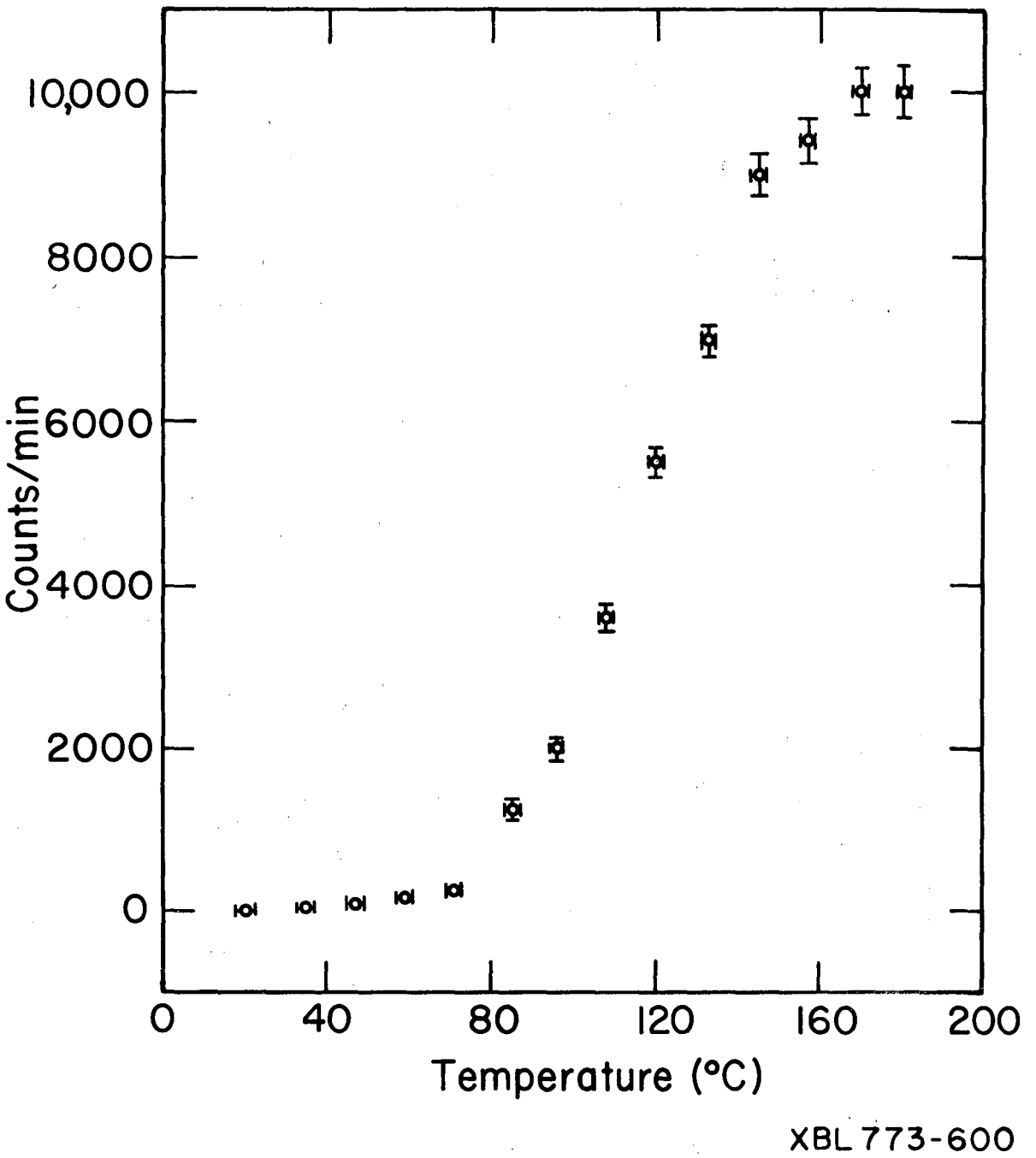
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Figure 4

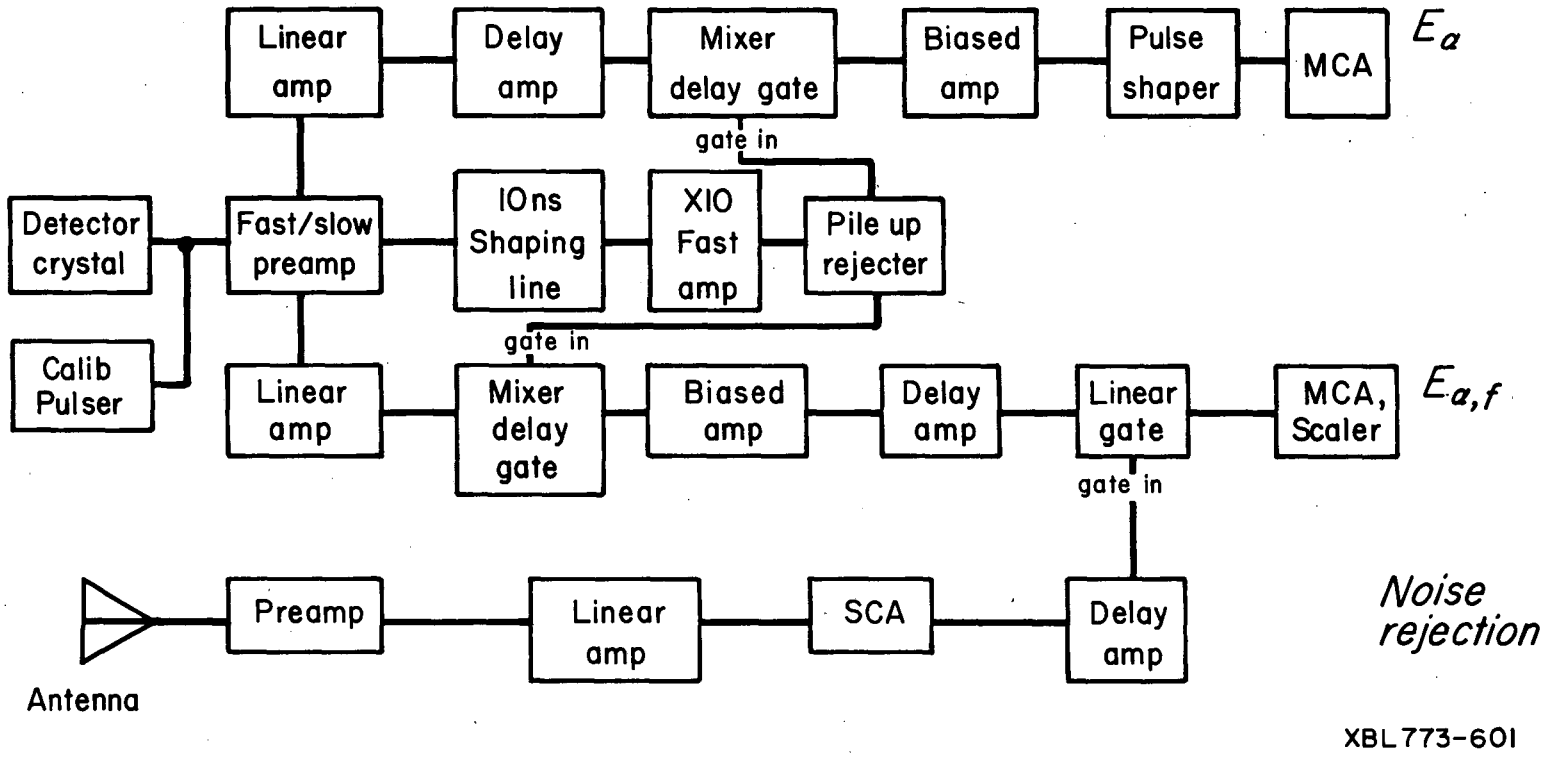

Figure 5

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
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