TIC

EG&G

EGG 1183-2355
S-111-TP

CONF-7702047--2

TRACE ELEMENT AND HYDROCARBON ANALYSIS OF MERCURIC IODIDE BY ION MICROPROBE AND X-RAY FLUORESCENCE TECHNIQUES

by
P.T. Randtke and J.L. Warren

JANUARY 1977

MASTER

SANTA BARBARA OPERATIONS
EG&G INC. 130 ROBIN HILL RD., GOLETA, CALIF. 93017

EGG 1183-2355
S-111-TP

TRACE ELEMENT AND HYDROCARBON ANALYSIS OF MERCURIC IODIDE BY ION MICROPROBE AND ELECTRON INDUCED X-RAY FLUORESCENCE TECHNIQUES*

by

P. Randtke and J. Warren
EG&G, Inc., Santa Barbara, California

ABSTRACT

Since 1971, research on mercuric iodide (HgI_2) crystals as nuclear radiation detectors has generated a growing interest in the semiconductor and crystalline properties of this material. An investigation pursued only recently pertains to the trace element and hydrocarbon impurities present in the raw HgI_2 starting material. While various purifying schemes have been employed, there is only a very limited understanding of their effectiveness. This paper describes studies undertaken with ion microprobe and electron x-ray fluorescence techniques 1) to quantify the trace elements in the residues removed from the starting material as well as in the final single crystals, and 2) to show the influence of impurity removal on nuclear detector performance. Both elemental and hydrocarbon contamination have been identified. The results indicate a preferred method of purification of the HgI_2 growth material.

---

*This work was performed under the auspices of the U.S. Energy Research and and Development Administration.

TRACE ELEMENT AND HYDROCARBON ANALYSIS OF MERCURIC IODIDE BY ION MICROPROBE AND X-RAY FLUORESCENCE TECHNIQUES*

by

P.T. Randtke and J.L. Warren
EG&G, Inc., Santa Barbara Operations
Goleta, California 93017

SUMMARY

Since 1971 the use of mercuric iodide (HgI_2) crystals as nuclear radiation detectors has generated a growing interest in the semiconductor and crystalline properties of this material. A recent investigation pertains to the trace element and hydrocarbon impurities present in the raw and purified HgI_2 growth material. While various purifying schemes have been employed, there is only a very limited understanding of their effectiveness. This paper describes studies undertaken with ion microprobe and x-ray fluorescence techniques to identify the trace elements in residues removed from the starting material and the final single crystals. Both elemental and hydrocarbon contamination have been identified. By employing both ion probe and x-ray fluorescence techniques on a given sample, a good separation of the hydrocarbon signal from the trace element signal can be achieved. Preliminary analysis results indicate a preferred method of purification of the HgI_2 growth material.

INTRODUCTION

Mercuric iodide has been studied and characterized by a variety of techniques including Laue x-ray diffraction and Lang x-ray topography,[1] etch pit density counts,[2] thermally stimulated conductivity measurements (TSC),[3,4] gamma ray spectroscopy,[5,6] charge carrier mobility/lifetime measurements,[7,8] and others. Another area

---

*This work was performed under the auspices of the U.S. Energy Research and Development Administration.

of investigation pursued only lightly is the trace element and other impurity analysis of single-crystal HgI_2. The influence of impurities on the performance of solid state radiation detection is well known from the literature. Some notable examples are the effects of trace amounts (ppb) of aluminum in high purity germanium[8] and indium and chlorine in cadmium telluride (CdTe).[9] In general, such impurities act as electronic traps for the charge carriers (holes and electrons) which are formed in the detector bulk by ionizing radiation. The loss of charge to these traps can cause severe degradation of gamma-ray spectral response (see Figs. 1a and b)

The intent of this paper is to describe some initial data on the trace element and hydrocarbon contamination of HgI_2 as determined by ion microprobe and x-ray fluorescence techniques.

TRACE ELEMENTS IN HgI_2

Preliminary studies of commercially available HgI_2 raw powder and residues from purified powder,[10] using optical emission and spark source mass spectrometry, have identified a whole host of impurities: Cu, Ag, Na, K, Si, Fe, Mg, Cs, Bi, Al, Cr, Na, Ni, Pb, Ba, B, Mn, and Sn. The source of these elements in the raw powder appears at this time to be in the manufacturing process. The commercial method of production, as noted in the literature,[11] involves the reaction of mercury and HCl to form a saturated $HgCl_2$ solution. The addition of KI precipitates out the HgI_2. Iodine, being highly reactive with most elements, easily reacts with a variety of contaminants in reaction vessel walls, storage containers, and the air.

HgI_2 PURIFICATION

Since mercuric iodide has a large vapor pressure (at 20°C – 5×10^{-5} torr; at 127°C – 0.2 torr), two rather elementary methods can be used for purification.[10] First, a zone-refinement technique involves a sealed pyrex tube of $\simeq$100 g of raw HgI_2 powder (backfilled with argon to atmospheric pressure) which is placed vertically in a holder. A heated (500°C) coil is slowly passed (20 hr/pass) around the tube upwards of 100 times from one end of the tube to the other. (We found there is a definite migration of impurities toward the lower end of the tube.)

The other purification method is vapor transport, where the HgI_2 powder is loaded into the sealed end of a 60-cm-long pyrex tube which is placed into a horizontal furnace (Fig. 2). The tube, which is pumped continuously to maintain a vacuum of about 25 microns is moved manually into the furnace hot zone (150°C) in steps of 2 cm/day, which entails about thirty repeated mini-sublimations, in order to transport the powder from one end of the tube to the other. HgI_2 purified in this manner is designated '30X' grade. This material is then manually removed and placed in a new tube so that the process can be repeated. This repeated sublimation is generally done four times (120X). Finally, the powder is placed into a special ampoule for single crystal growth.[12] This second technique has been found to be more satisfactory for practical crystal growth.

Both methods would normally suffice to give a very high purity end product, since the temperatures involved are far below the melting point of most of the individual contaminants, and the vapor pressure of the elemental impurities is much lower than that of HgI_2. However, iodine is notorious for forming tri- and tetra-iodides with many metals,[13] and the melting points of such compounds fall well within the range of the purifying furnace temperature, i.e., SiI_4, M.P. = 122°C. A substantial amount (30 mg per 100 g of HgI_2) of blackish-brown residue is always left at the initial starting point of the 30X purification (Fig. 3), but only occasionally is it noticeable in subsequent purifications. Therefore, it can be assumed that most of the low vapor pressure impurities are removed in the first few mini-sublimations, while the rest tend to migrate in various ways with the bulk of the HgI_2 powder, possibly as multi-iodated compounds.

RESIDUE ANALYSIS — ELEMENTAL

To document various raw starting material batches and pinpoint their main impurities, we analyzed in detail the residue left from various purifying runs. The ion microprobe and x-ray fluorescence techniques were the chosen analytical methods. The ion microprobe mass analyzer (IMMA)* was used in all microprobe measurements. Basically, a beam of 13.5 keV $^{16}O^-$ ions is made to impact in a raster-like pattern on the sample surface in a vacuum of about 10^{-7} torr. The interaction of the oxygen ions with the specimen ionizes the elements and hydrocarbons in the sample. An electrostatic focusing column then draws this ionized debris into a mass spectrometer, for exact identification of the mass to charge ratio (m/e).

---

*Applications Lab., ARL Inc., Sunland, California

The spot size sampled can be small as the cross-section of the $^{16}O^-$ beam, i.e., <2 μm. In these analyses, a 100 μm × 100 μm raster pattern was used.

The samples were prepared as follows. A small mass (~1 μg) of residue was separated from the main residue sample (Fig. 4) and placed between two small sheets (5 mm × 10 mm × 0.25 mm) of high purity indium foil. The sheets were pressed together, embedding the residue into the surfaces of the indium. The foils were then separated and the sample was ready for analysis. The samples were not coated originally, but it was later found that there was enough electrostatic charging from the ion beam such that a 100Å layer of palladium was needed to neutralize the sample.

A brief description of the samples is as follows:

Sample 1 – Analysis of typical indium foil in which the residue was embedded.

Sample 2 – 30X residue (9/8/76) – a typical black fibrous residue left over from open vacuum sublimation of raw material.

Sample 3 – 120X residue – the HgI_2 was treated with excess I_2 at this stage of purification. Apparently, this triggered the appearance of an additional amount of residue.

Sample 4 – 30X run on new furnace – light brown fibrous residue from the initial run of a new horizontal tube furnace.

Sample 5 – 30X residue (typical).

Sample 6 – 60X synthetic – black residue from a 60X purification an HgI_2 made at EG&G, Inc. (30X residue not available for analysis).

Sample 7 – 30X residue (typical).

Sample 8 – 30X residue (typical, used in analysis discussed below).

The results of the analysis are given in Table 1, but a brief discussion of the various assumptions and corrections made to the raw data is necessary. Since the ion probe does not have a uniform sensitivity response to the various elements of interest, correction was made according to published results[14] on the IMMA's response to pure elements. Important matrix effects could not be accounted for. Also, only the predominant isotope for a particular element was quantitatively measured, and therefore correction for the full isotope abundance was made. Since there was no internal standard or dopant in the residue, the IMMA's stability was accounted for by monitoring fluctuations in the $^{16}O^+$ signal from the sample which was induced by the incoming $^{16}O^-$ beam. Correction for incomplete coverage of the indium substrate by the sample and also the subsequent contribution of the various

indium contaminants (see Sample 1, Table 1) to the sample response were made by monitoring the intensity of the indium isotopic signal (this assumes little or no indium contamination in the sample).

Table 1 gives the relative mass contribution (in percent) for each of the elements listed. For example, Sample 3 shows a level of 98% carbon. This means that, of all the elements listed in Table 1, carbon constituted 98% of the sample seen in the 100 μm × 100 μm spot. Hydrocarbon contaminants, reaction products, hydrides, and others are not accounted for. Table 1 also includes data on Li, F, Na, Cℓ, and K. Instrument corrections for these elements are not available, but the fact that they were detected is important.

The most striking feature of the Table 1 data is the similarity between Sample 2, 4, 7, and 8, all 30X residues. Sample 5, also 30X, exhibited the lowest percentages for its elemental content. The carbon and silicon values are surprisingly low, but apparently there was a large amount of silver present (amalgamation with the Hg?) — upwards of 8 times greater than the next highest value. The highest relative carbon percentages were found in the 60X (89%) and 120X (92%) residues. Assuming that the above corrections to the data are valid, the predominant impurities appear to be: C, Si, Aℓ, Ca, Fe, Cu, and Ag. In addition, Na, Cℓ, and K from the bottom of Table 1 appeared worth investigating.

RESIDUE ANALYSIS — HYDROCARBON

All of the residue samples showed some evidence of hydrocarbon contamination. Figures 5a and b shows the relative signal intensity versus (m/e) ratio for Samples 2, 4, 7, and 8, all 30X residues. Sample 5, also 30X, exhibited the lowest the latter brown. Note the high density of mass peaks on the 10X scale for Sample 4. Close examination of Figure 5a reveals that these peaks are associated with other than elemental species and are most probably due to contamination. Sample 2 is relatively free of such material. A rough estimation shows the signal peak density in the data for Sample 4 to be twice that of Sample 2. The source of this contamination has not been identified. An early suspicion was that the problem originated with the vacuum system; however, a molecular sieve trap and a liquid nitrogen cold trap precede the evacuation line from the mechanical roughing pump, which is used in continually evacuating the purification tubes during vapor transport purification.

X-RAY FLUORESCENCE ANALYSIS

Because of the possible interference of elemental isotope signals by hydrocarbon signals, and the interest in developing a complementary technique of analysis, x-ray fluorescence was investigated as a diagnostic method. A new set of residue samples, primarily from 30X material, was analyzed using a Finnigan Quanti/Matrix QM900A* system having a rhodium target x-ray source tube (15 kV). The samples were pressed into Lexan cups (Fig. 6) and a 10 μm layer of polypropylene was stretched over the top. Seven samples were examined, and the results are given in Table 2. The data are given in ppm levels, based on the data from the NBS Glass Standard (500-ppm) (Sample 8). The HgI_2 powder could not be analyzed by this method, because the signals from the Hg and I are so large as to suppress the smaller signals from the trace contaminants. Figures 7a and b show the graphs of the energy spectral data taken on Samples 3 and 4.

Table 2 includes analysis of an empty lexan cup (Sample 7) and an NBS glass standard (Sample 8). The empty cup showed only traces of calcium and iron. All the residue samples were similar except for Sample 4, a 90X purification. In general, the residues contained major amounts of mercury, iodine, potassium, and iron, as well as trace amounts of Si, Cu, and Zn. Sample 4 contained no potassium or zinc and less iron and copper than the other residues. This conforms closely to the ion probe analysis, although the IMMA appears to have a better sensitivity for more trace elements. The ppm levels are only given for elements which are so noted in the NBS standard run. Otherwise, only the count data for a particular elemental peak are given.

SPECIFIC TRACE ELEMENT REDUCTION

The above results were preliminary to an attempt to reduce the levels of specific impurities in the HgI_2. We decided to try to lower or eliminate the aluminum content by the following method. Approximately 400 g of commercial HgI_2 powder was purified to the 30X stage. This batch was then separated into four equal parts, and each 100 g was then processed to the 120X stage by the following procedures.

Run 1 — A control run done by the usual techniques. The purification tubes were continuously pumped.

---

*Analysis done at SEAL, Inc., Los Angeles, California 90066

Run 2 — At the 60X stage, 0.87 g of HgO was added in an attempt to cause oxide reaction products with trace amounts of aluminum impurity. Also, the purification tubes were sealed and not continuously pumped. The 90X and 120X runs were done with closed tubes.

Run 3 — At the 60X stage, the tube was evacuated to $\simeq 10\mu$ and backfilled with argon to about 100μ pressure and sealed. Runs at 90X and 120X were done the same.

Run 4 — At the 60X stage, the purification tube was backfilled to 100μ with O_2, and at the 90X stage to 100μ with HCℓ vapor and sealed. The 60X, 90X, and 120X runs were done in closed tubes. The O_2 and HCℓ were intended to further create reaction products with the aluminum and perhaps the Na and K.

Samples were taken of the raw unpurified HgI_2 powder, the residue left after the 30X stage, and the final 120X purified powders. There were no noticeable residues left in any of the stages of purification greater than 30X.

All analyses on these samples was performed using the ion microprobe. In addition, the residue was also analyzed by x-ray fluorescence. The results are shown in Table 3. Only eight elements were selected for study on these samples: C, Na, Aℓ, Si, K, Ca, Cr, and Fe. Lexan cups were fabricated and the powder pressed into their interiors (Fig. 6). The top surfaces were then flashed with palladium. The residue sample was prepared as described above, and its results are shown as Sample 8 in Table 1. Fortunately in the case of the HgI_2 powder, either the Hg or I signal can be used to monitor the IMMA instrument stability. In these samples the ^{127}I isotope was used, since its signal was much larger than any of the Hg isotopes. The control run (Run 1) shows appreciably higher percentages for all the elements studied. The various additives in Runs 2, 3, and 4 did not seem to give the expected specific reduction in all the contaminants. Run 2 recorded higher values of Aℓ, K, and Ca, while Run 3 had higher values for Na, Si, K, Ca, and Cr. Run 4 showed reductions in C, Na, Aℓ, and Fe. Perhaps these reductions were due more to the elevated pressures in the sealed tubes than the variation on the additives. Assuming that most of the volatile hydrocarbons are removed at the 30X stage, then the outgassing at later stages in the sealed tubes is due primarily to adsorbed gases (especially oxygen) on the powder. The addition of the argon, oxygen, and HCℓ only tended to heighten this effect. Certainly the presence of only adsorbed oxygen in the sealed tubes, as well as the increased pressure of vaporization, could provide a favorable environment for making various reaction products which would remain behind.

Since the impurity levels involved are at the ppm level such trace residue could still be left behind in the sublimation process, even though they are not visible.

CONCLUSION

A number of trace elements and evidence of hydrocarbon contamination have been identified in various purity levels of HgI_2. A reliable method of analysis by the ion microprobe technique has been developed for studying relative concentration levels. Finally, some success has been achieved in reducing the level of several of the trace elements. Further work on linking the effect of these reductions to final detector performance will be done, as well as studying new purification techniques to reduce all trace impurities.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. T. Whatley and D. Comafort of ARL for assistance with the ion microprobe analysis and Dr. L. Kashar of Seal, Inc., for help with the x-ray fluorescence analysis.

REFERENCES

1. P.T. Randtke and C. Ortale, *IEEE Trans. Nucl. Sci., NS-25*, to be published February 1977.

2. J.P. Pon Pon, R. Stuck, P. Siffert, B. Mayer, C. Schwab, *IEEE Trans. Nucl. Sci., NS-22*, 182 (February 1975).

3. Yacomby, et al, *IEEE Trans. Nucl. Sci., NS-25*, to be published February 1977.

4. R. Whited and L. van den Berg, *IEEE Trans. Nucl. Sci., NS-25*, to be published February 1977.

5. J. Llacer, et al, *IEEE Trans. Nucl. Sci., NS-21*, 305 (February 1974).

6. M. Slapa, et al, *IEEE Trans. Nucl. Sci., NS-23*, 102 (February 1976).

7. P.T. Randtke, C. Ortale, R.C. Whited, and L. van den Berg, *Proceedings of ERDA Symposium on X-Ray and Gamma-Ray Sources and Applications*, Ann Arbor, Michigan, 71-74 (May 1976).

8. E. Haller and W. Hansen, *IEEE Trans. Nucl. Sci., NS-21*, 279 (February 1974).

9. C. Barnes and K. Zanio, *IEEE Trans. Nucl. Sci., NS-23*, 177-179 (February 1976).

10. "SANDS R&D Program FY74 Progress Report," EGG 1183-2305, 1-5 to 1-7 (1975).

11. *Gmelins Handbuck der Anorganishen Chemie, Volume 34-B2.*

12. M. Schieber, W.F. Schnepple, and L. van den Berg, *J. Cryst. Growth, 33*, 125-135 (1976).

13. R. Rolsten, *Iodide Metals and Metal Iodides*, John Wiley and Sons, Inc., New York (1961).

14. C.A. Andersen and J.R. Hinthrone, *Science, 175*, 854 (February 1972).

Table 1. Relative mass contribution (%) for element samples

Element	Mass Number	Residue Sample Results (relative percentage)							
		1	2	3	4	5	6	7	8**
B	11	0.0056	0.023	0.0085	0.19	0.0081	0.0049	0.13	---
C	12	12.22	85.33	97.77	56.25	47.06	98.67	65.22	89.52
Mg	24	0.20	0.45	0.31	1.20	0.081	0.039	2.17	---
Aℓ	27	6.22	3.33	1.04	20.31	0.49	0.19	10.29	3.62
Si	28	3.78	4.00	0.51	3.44	13.09	0.076	5.36	2.61
Ca	40	0.015	0.45	0.068	2.03	0.022	0.099	1.74	1.04
Ti	48	0.098	0.053	0.0044	0.14	0.00043	0.0000	0.071	---
Cr	52	0.0011	0.028	0.043	0.056	0.00071	0.058	0.042	0.028
Fe	56	0.38	2.40	0.084	9.22	0.053	0.32	5.22	3.19
Cu	63	0.14	0.41	0.020	1.88	0.14	0.037	3.62	---
Ag	107	0.024	3.47	0.0058	5.00	39.71	0.085	5.07	---
In*	115	77.78	---	---	---	---	---	---	---
Sn	120	0.27	0.041	0.041	0.19	0.0068	0.053	0.88	---
Ba	138	0.00071	0.0037	0.00034	0.017	0.00016	0.00089	0.020	---
Pb	208	0.0000	0.020	0.0032	0.17	0.0079	0.029	0.39	---
Totals (%)***		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
(Other elements detected for which corrections are not available.)									
Li	7	M	H	M	H	M	L	H	-
F	19	M	M	L	H	L	H	H	-
Na	23	L	H	M	H	M	H	H	H
Cℓ	35	L	M	L	H	M	M	H	-
K	39	L	M	M	H	M	M	H	H

*Tabulated only for Sample 1 — pure indium substrate.

**Only a select few elements were analyzed in this sample. The combined sum of the other elements was less than 5%, relative amount.

***IMMA instrument corrections could not be made for other elements listed below.
Legend: Relative values are L = low, M = medium; H = high

Table 2. Results of residue analysis by x-ray fluorescence

	ELEMENT						
	Si	Hg	K	I	Fe	Cu	Zn
Run 1 — 30X							
Relative	1136	19517	8746	94401	23231	2258	2690
ppm	11453	-	-	-	7987	805	1433
Run 2 — 30X							
Relative	1092	17794	10112	80680	22537	1930	1673
ppm	11010	-	-	-	7105	668	1037
Run 3 — 30X							
Relative	1243	23162	10421	102727	20803	1883	1469
ppm	12531	-	-	-	6538	649	759
Run 4 — 90X							
Relative	658	24282			7973	479	158
ppm	6634	-	-	-	2341	77	35
Run 5 - 90X							
Relative	990	14836	11551	93315	24004	2189	1888
ppm	9951	-	-	-	8242	774	990
Run 6 — 90X							
Relative	970	18337	16600	74988	24479	1812	1729
ppm	9780	-	-	-	7741	620	903
Lexan Cup							
Relative	0	0	82	0	1228	437	142
ppm	0	-	-	-	1633	581	189
NBS Standard							
Relative	66693	0	0	0	2800	2178	832
ppm	336200	-	-	-	458	444	433

Table 3. Relative concentrations of trace elements (see text)

Elements	Raw Powder	Run 1	Run 2	Run 3	Run 4
C	0.51	0.027	0.00043	0.00046	0.00015
Na	7.03	0.88	0.0077	0.0045	0.036
Aℓ	0.83	0.075	0.030	0.0087	0.011
Si	0.50	0.037	0.0087	0.013	0.084
K	1.94	0.860	0.016	0.026	0.054
Ca	1.04	0.041	0.0019	0.0027	0.0049
Cr	0.21	0.0034	0.0016	0.0013	0.00020
Fe	0.41	0.0088	0.0060	0.0060	0.0022

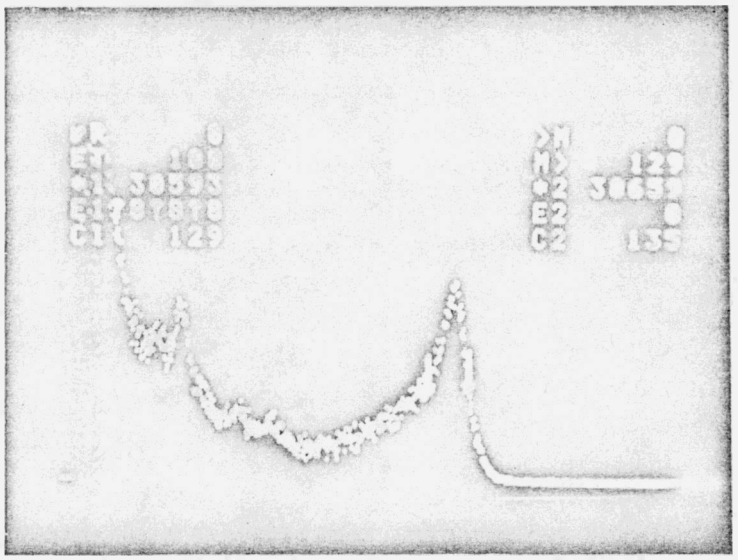

Fig. 1a. ^{241}Am pulse height spectrum from HgI_2 detector. Note the severe hole trapping which distorts the low energy side of the 59.6-keV photopeak.

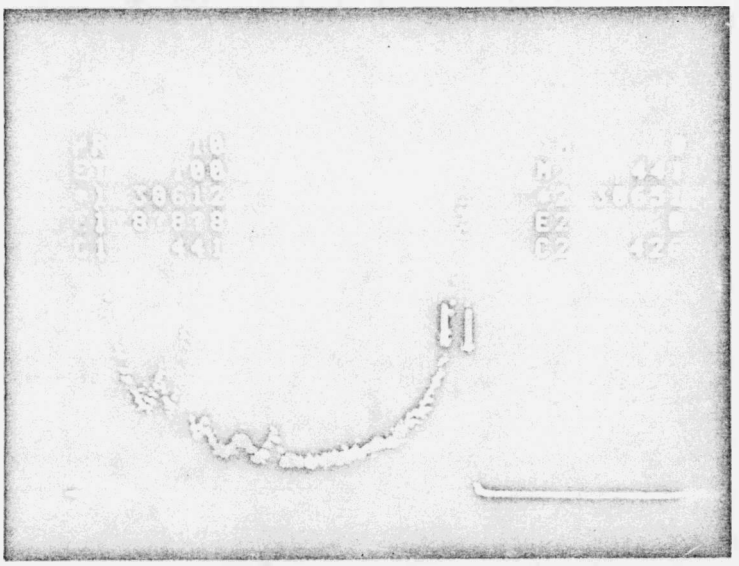

Fig. 1b. ^{241}Am pulse height spectrum from a HgI_2 detector. The resolution of the 59.6-keV peak is improved due to low hole trapping.

4585

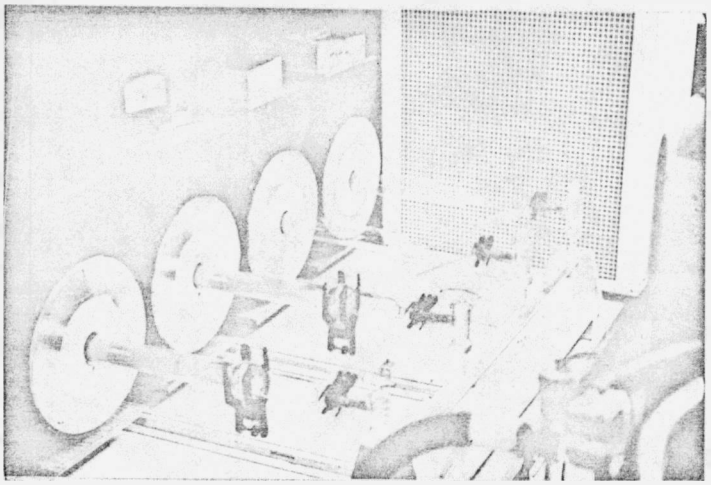

Fig. 2. View of four horizontal furnaces with purifying tubes at various stages of processing.

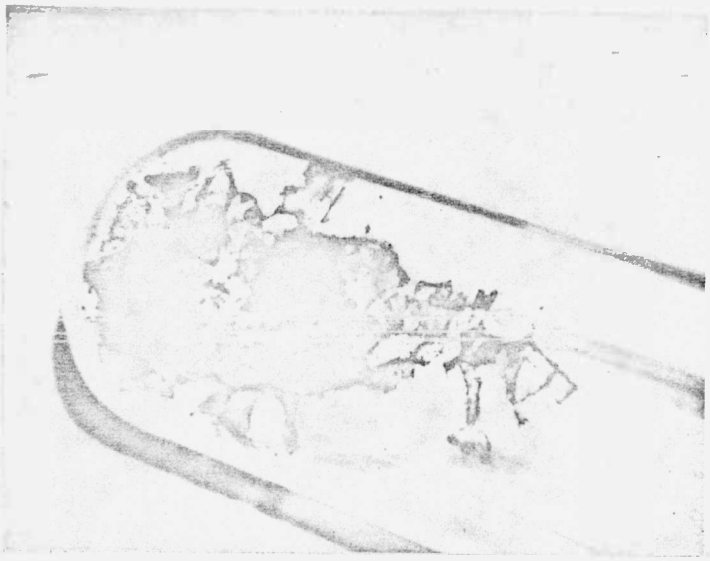

Fig. 3. View of starting end of purifying tube after a 30X run. Note the large amount of residue.

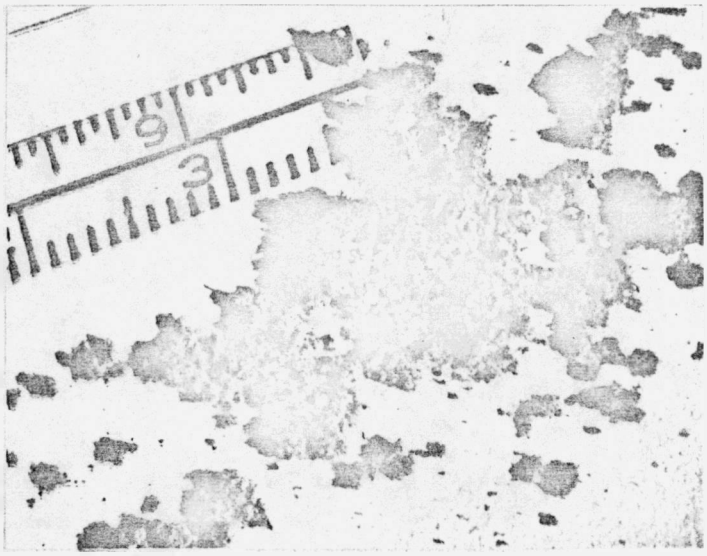

Fig. 4. Closeup of residue removed after at 30X run.

4586

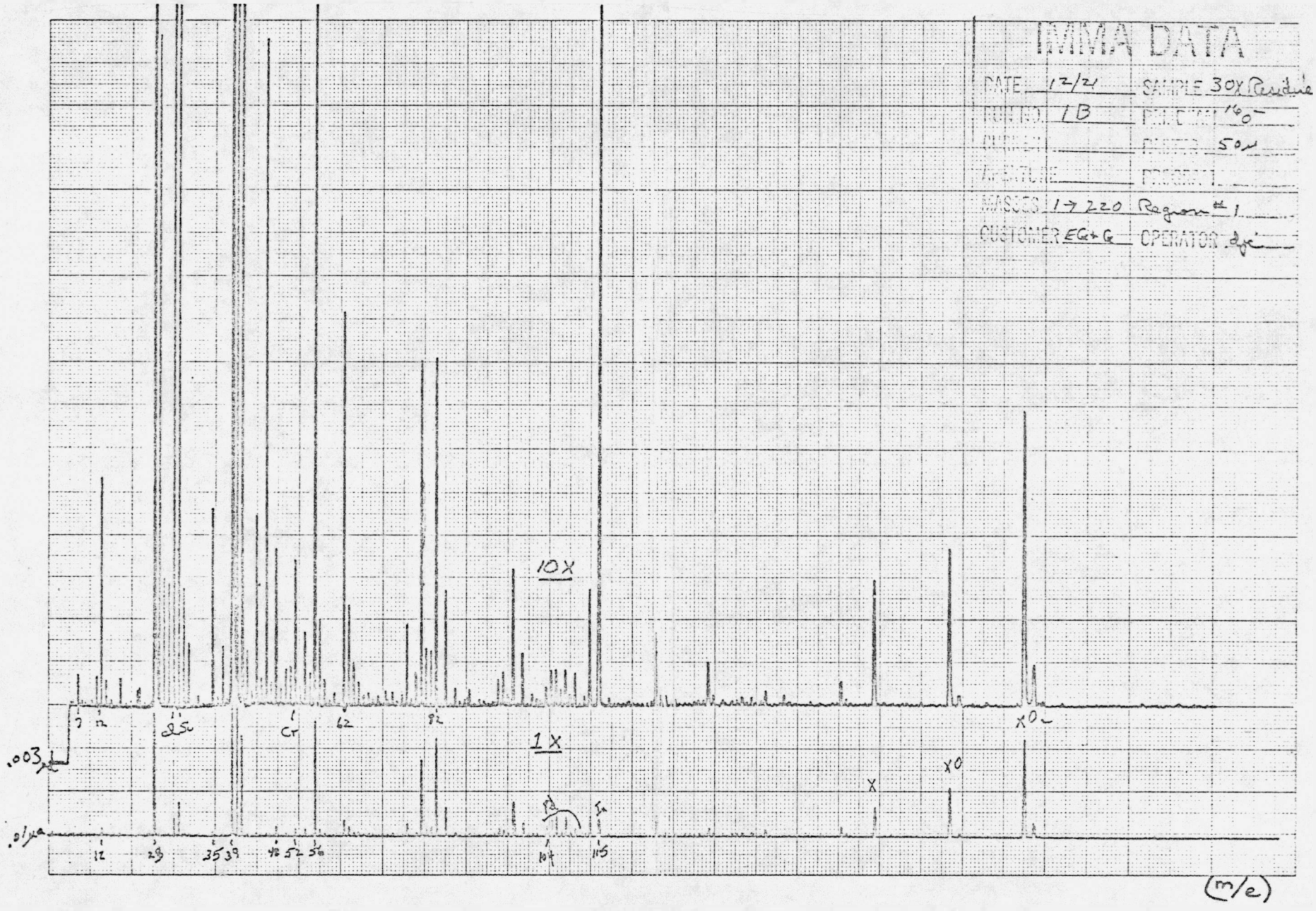

Fig. 5a. Mass spectroscopic output from ion-microprobe (IMMA). Residue sample has a high hydrocarbon content.

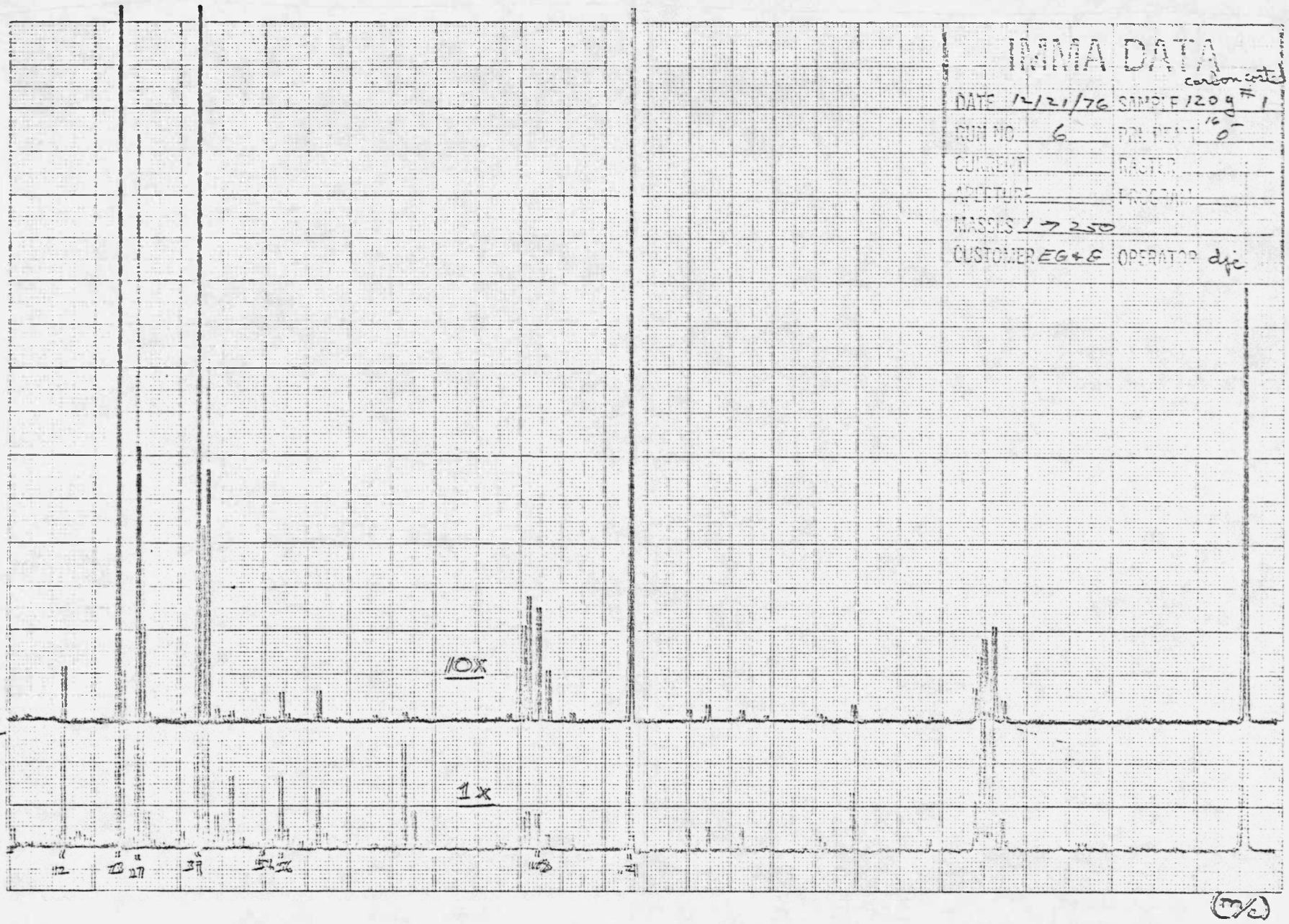

Fig. 5b. Mass-spectroscopic output from ion-probe (IMMA). Residue sample has a low hydrocarbon content.

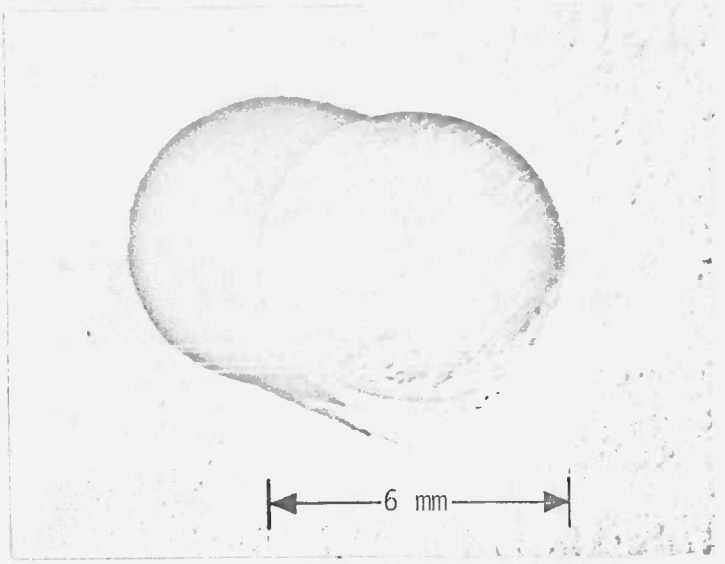

Fig. 6. Lexan cup holder for HgI_2 powder samples.

4589

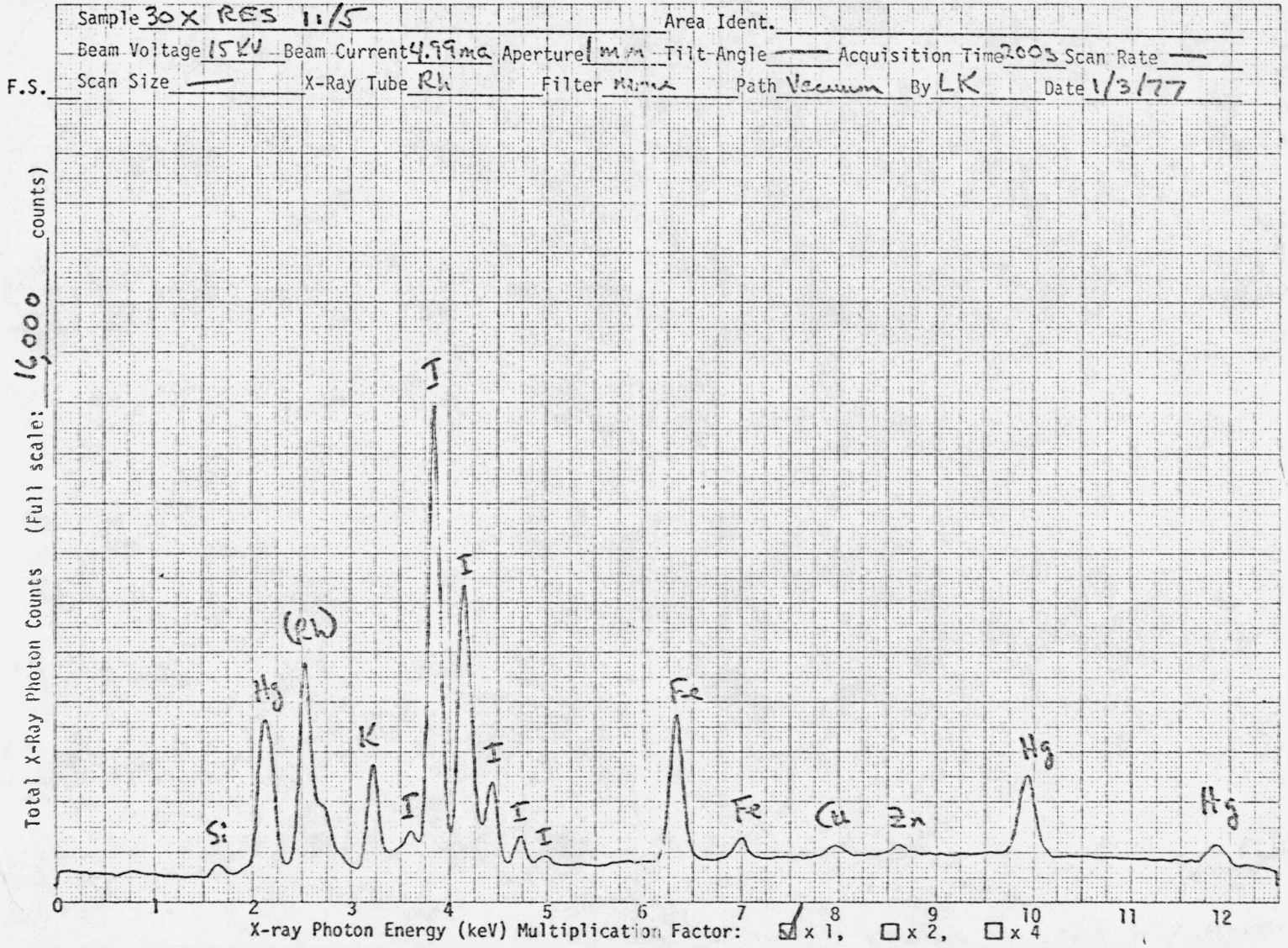

Fig. 7a. X-ray fluorescence spectral data on Sample 3 in Table 2. 200 second acquisition time.

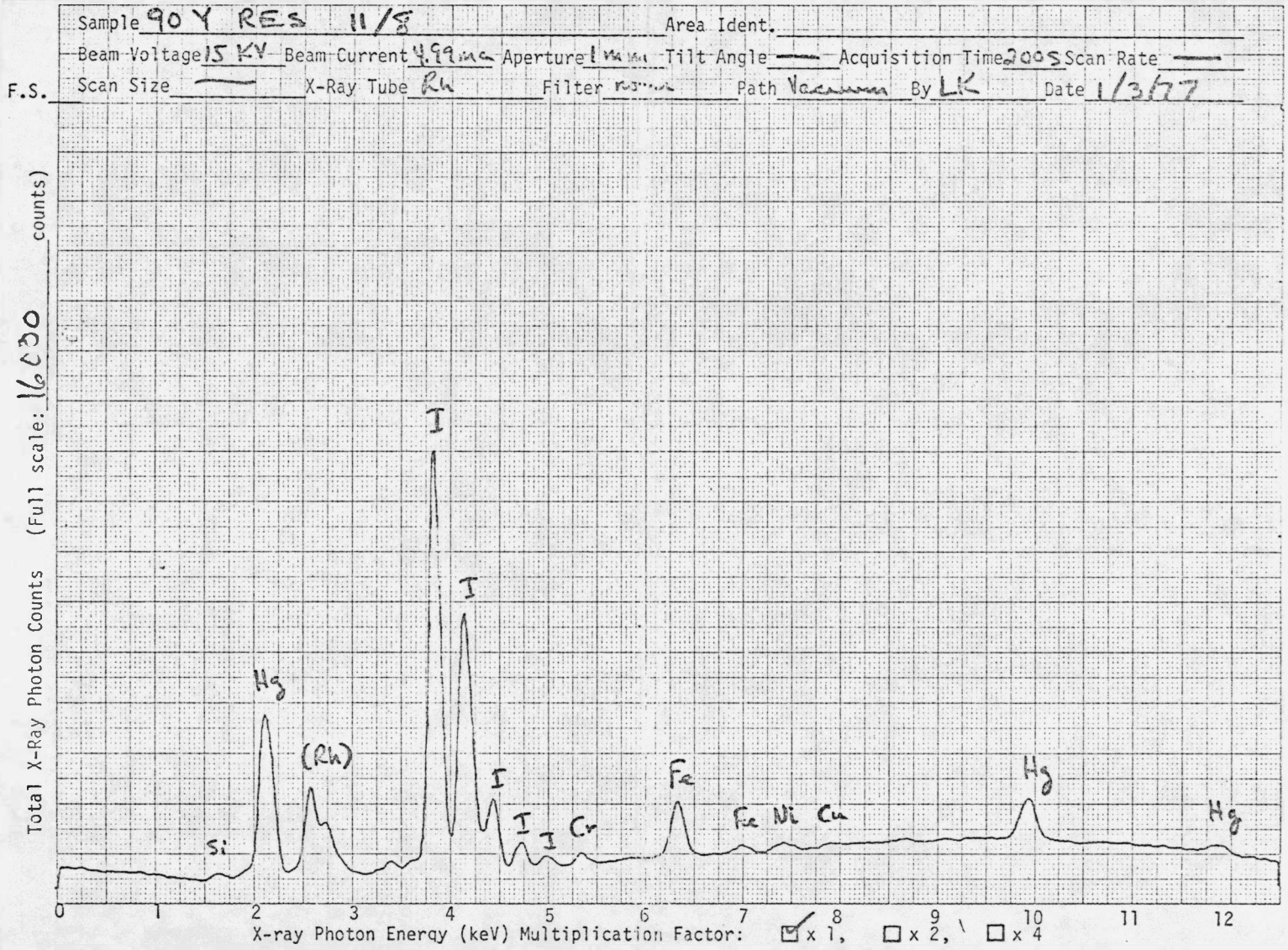

Fig. 7b. X-ray fluorescence spectral data on Sample 4 in Table 2. 200 second acquisition time.