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Y/DW--538

Date of Issue: October 15, 1984

DE91 006302

CLEANING OF URANIUM VS MACHINE COOLANT FORMULATIONS

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Prepared for the Department of Energy
Under Government Contract DE-AC05-84ØR21400

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Summary

This study compares methods for cleaning uranium chips and the residues left on chips from alternate machine coolants based on propylene glycol-water mixtures with either borax, ammonium tetraborate, or triethanolamine tetraborate added as a nuclear poison. Residues left on uranium surfaces machined with perchloroethylene-mineral oil coolant and on surfaces machined with the borax-containing alternate coolant were also compared.

To summarize the chip cleaning findings:

(1) Ammonium tetraborate coolant left the uranium surfaces easiest to clean.
(2) Storage in coolant increases difficulty of boron removal.
(3) Storage in Freon does not remove boron from the surface but does make boron removal easier compared with storage in coolant.
(4) After storage in the sodium tetraborate coolant, ultrasonic cleaning in K_2CO_3/H_2O_2 was most effective in boron removal. After storage in Freon, ultrasonic cleaning in demineralized water was equally effective.
(5) Oakite soaking helped reduce boron residues on samples subsequently ultrasonically cleaned in demineralized water.
(6) After storage in ammonium tetraborate coolant, soaking in Oakite and ultrasonic cleaning in 80°C demineralized water was most effective. This treatment resulted in the cleanest sample overall with low boron residual.

In comparing machined surfaces, greater chlorine contamination was found on the surface of the perchloroethylene-mineral oil machined surfaces, but slightly greater oxidation was found on the surfaces machined with the alternate borax-containing coolant. Overall, the differences were small and a change to the alternate coolant does not appear to constitute a significant threat to the integrity of machined uranium parts.

Introduction

The use of perchloroethylene as an ingredient in coolants for machining of enriched uranium at the Oak Ridge Y-12 Plant* has to be discontinued due to environmental concerns. Thus an alternate coolant of propylene glycol-water with sodium tetraborate (borax) added as a nuclear poison was devised. It is important that both machined surfaces and machine turnings or chips be cleaned with as little residue of boron as possible, as a buildup of boron in the recycled uranium is undesirable. Thus this study compares various cleaning methods for cleaning uranium chips, the residues left on chips from three coolants using different tetraborates, and the residues left on uranium surfaces machined with perchloroethylene-mineral oil versus surfaces machined with the alternate coolant.

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* Operated for the U. S. Deparment of Energy by Martin Marietta Energy Systems, Inc.

Prior Work

Development of the propylene glycol-water-borax coolant for machining fissile materials has been reported.

Presentation of Experimental Work

Comparison of Cleaning Methods on Uranium Turnings and Chips

Uranium turnings or chips have a high surface area to volume ratio and thus surface residues have a more serious effect in contributing to contamination of recycle material than do large parts. Machine turnings also have a "shiny" and a "dull" side. The "shiny" side is the smoother side which separates from the base metal. The outer "dull" side is rougher and more heavily oxidized.

Uranium turnings from machining operations using three different coolants were cleaned by several methods. The resultant surfaces were analyzed using an ARL Ion Microprobe Mass Analyzer (IMMA) which is a secondary ion mass spectrometer (SIMS) with microprobe capabilities. Table I lists the sample types and the cleaning methods applied. Propylene glycol and water are a constant in all three of the coolant solutions.

The effectiveness of the cleaning methods were compared in three ways. One method was to run comparison secondary ion mass scans of areas 280 x 350 μm sputtered with a 5 nA, N_2^+ ion beam. CARISMA, a computer program, was used to calculate atom percent abundance of boron, sodium, calcium, potassium, and uranium. CARISMA is not accurately quantitative in an unknown matrix, but should give reasonable relative values in similar matrices. A second method was secondary ion imaging. This is not a good quantitative method, but is good for determining distributions. The third technique was secondary ion depth profiling to determine depth of surface contamination.

Table I. Sample, Coolant, Cleaning Method

Sample	Coolant	Storage Time (days)	Cleaning
1113	$Na_2B_4O_7$	10	Ultrasonically Cleaned (US) in Demineralized Water (DW)
1114	$Na_2B_4O_7$	10	US in 5-10% HNO_3/ 1% H_2O_2
1115	$Na_2B_4O_7$	10	US in 1% Mannitol/ 1% NaOH; 5 rinses
1116	$Na_2B_4O_7$	10	US in 5% K_2CO_3/ 1% H_2O_2; 5 rinses
1123	$Na_2B_4O_7$	35	US in 50% Acetone/50% DW; Acetone rinse
1124	$Na_2B_4O_7$	35	US in 20% Methanol/50% DW; 20% Methanol rinse
1125	$Na_2B_4O_7$	20 (in Freon)	None
1128	$Na_2B_4O_7$	20 (in Freon)	US in DW; returned to Freon
1129	$Na_2B_4O_7$	3 (in Freon)	US in DW; US in Freon; US in 1% HNO_3
1118	$(NH_4)_2B_4O_7$	3	Soak* in 5% Oakite; US in DW; Isopropanol dried
1119	$(NH_4)_2B_4O_7$	3	Soak* in 5% Oakite; US in 1% Mannitol/NH_3 (pH 11); Isopropanol dried
1120	$(NH_4)_2B_4O_7$	5	Soak* in 5% Oakite; US in 1% $(NH_4)_2CO_3$ + H_2O_2; Rinse in DW; Isopropanol dried
1126	$(NH_4)_2B_4O_7$	19	15 minutes in 70°C DW; US in 70°C DW; 2 rinses; Acetone dried
1127	$(NH_4)_2B_4O_7$	19	US in 22°C DW twice; Acetone dried
1130	$(NH_4)_2B_4O_7$	20	Soak* in 5% Oakite at 20°C; US in 20°C DW
1131	$(NH_4)_2B_4O_7$	20	Soak* in 5% Oakite; US in DW at 80°C
1132	Triethanol-amine tetra-borate	25 minutes	US in DW
1136	Triethanol-amine tetra-borate	3	US in DW

* Ten minutes

A brief survey of all the samples using mass scan data with CARISMA-determined values for boron is shown in Table II. Figures 1-5 are bar plots of boron, sodium, potassium, and calcium surface contaminants on the smooth sides only as determined by CARISMA. These numbers are reported as atom percent with three qualifications: 1) The abundance of the elements boron, sodium, calcium, potassium, and uranium were assumed to add to 100%; 2) some sputtering, thus removal, of surface contamination occurs before the peaks are recorded; and, 3) CARISMA calculated values are sometimes inaccurate by factors of 2 to 5.

The survey values from Table II indicate that the rough side generally retains more boron after cleaning than the smooth side. The $(NH_4)_2B_4O_7$ coolant generally left less boron on the smooth sides but apparently more boron on the rough sides than the $Na_2B_4O_7$ coolant. However, the rough side difference is probably an anomaly caused by the conditions of the machining. The $Na_2B_4O_7$ coolant was sprayed onto the parts in the normal manner, whereas, the $(NH_4)_2B_4O_7$ coolant was poured by hand from a bottle during the machining since only small batches were made for testing. The result was that the chips got hotter and the rough sides were rougher and more heavily oxidized than normal. Thus, the rough side values of the $(NH_4)_2B_4O_7$ coolant machined chips are not expected to be truly representative of typical machining operations.

Samples 1113 and 1116 are good examples of the boron level extremes observed. Sample 1113 was ultrasonically cleaned using only demineralized water at room temperature. Sample 1116 was ultrasonically cleaned in a 5% K_2CO_3/1%H_2O_2 solution. This solution appeared to be one of the more effective ones for cleaning boron from the $Na_2B_4O_7$ coolant machined turnings or chips. Figure 6 shows a secondary ion image of boron on the smooth side of sample 1113. Heavy islands of boron were found which totally obscured the uranium under them. Figure 7 shows sodium in the same area. The boron rich areas are also rich in sodium. Figure 8 shows a boron image from sample 1116. Boron traces are still found scattered over the surface, but not in heavy islands. A sodium image of the same area in Figure 9 shows much less sodium than on sample 1113. However, potassium residues were abnormally high. Calcium, barium, and, in some areas, iron or titanium impurities were also found.

Secondary ion depth profiles of boron in Figures 10A and 10B show the difference in relative boron depth between the heavy-deposit islands shown in Figure 6 and a typical area on the smooth surface between islands. A boron profile from sample 1128 in Figure 11 shows the usual rapid drop in boron as a well-cleaned surface is sputtered. Unfortunately, no surface profilometer is available in our laboratory to quantify depths of unusual materials such as these boron-containing islands.

Table II. Boron Values (Atom %) Determined by CARISMA from Mass Scans of Surfaces.

Sample	Smooth Side	Rough Side
$Na_2B_4O_7$		
1113	1.74	*
1114	1.81	*
1115	0.25	0.27
1116	0.14	*
1123	0.55	0.99
1124	0.63	0.61
1125	24.5	29.9
1128	0.16	0.40
1129	0.15	0.18
$(NH_4)_2B_4O_7$		
1118	0.19	0.47
1119	0.44	0.79
1120	0.24	0.47
1126	1.46	1.56
1127	0.72	1.03
1130	0.20	1.21
1131	0.09	1.58
Triethanolamine		
1132	0.38	*
1136	1.07	*

* Not run

The effect of storage in Freon rather than in machine coolant is illustrated by samples 1125, 1128, and 1129. Sample 1125 was stored in Freon and not further cleaned before measurement. Deposits of boron and sodium were found to be very heavy on this sample. The CARISMA-determined boron was 25 atom percent (same assumptions as listed previously) on the surface. However, ultrasonic cleaning in distilled water effectively reduced the boron levels on these samples. An additional cleaning in 1% HNO_3 further reduced the impurities sodium, potassium, and calcium (see Figure 2). Thus, storage in Freon does appear to allow easier removal of boron than storage in the machine coolant.

Quick removal of the uranium from the coolant versus storage in coolant before cleaning is illustrated by samples 1132 and 1136. The samples were machined under a coolant containing triethanolamine tetraborate. Sample 1132 was removed after 25 minutes and sample 1136 after 3 days. Both were ultrasonically cleaned in room temperature demineralized water. From Figure 6, it is seen that the longer exposure resulted in less effective cleaning.

Soaking in Oakite prior to ultrasonic cleaning in demineralized water was found to be effective in reducing the boron residues left by the ammonium tetraborate coolant (see Figure 4).

A comparison of the relative ease of cleaning samples from the sodium tetraborate, ammonium tetraborate, and triethanolamine (TEA) tetraborate machine coolants is shown in Figures 12 and 13. All of these samples were cleaned ultrasonically in room temperature demineralized water. Figure 12 shows the high sodium residues found typically on sodium tetraborate coolant samples. The Y-axis scale is spread in Figure 13 to more graphically show the other elements. This data indicates that use of ammonium tetraborate rather than sodium tetraborate would make cleaning of uranium surfaces easier.

To summarize the chip cleaning findings:

(1) Ammonium tetraborate coolant left the uranium surfaces easier to clean than those containing either borax or triethanolamine.
(2) Storage in coolant increases difficulty of boron removal.
(3) Storage in Freon does not remove boron from the surface but does make boron removal easier compared with storage in coolant.
(4) After storage in the sodium tetraborate coolant, ultrasonic cleaning in K_2CO_3/ H_2O_2 was most effective in boron removal. After storage in Freon, ultrasonic cleaning in demineralized water was equally effective.
(5) Oakite soaking helped reduce boron residues on samples subsequently ultrasonically cleaned in demineralized water.
(6) After storage in ammonium tetraborate coolant, soaking in Oakite and ultrasonic cleaning in 80°C demineralized water was most effective. This treatment resulted in the cleanest sample overall with low boron residual.

Comparison of Uranium Surfaces Machined With New and Old Coolants

A comparison of surface residues and/or corrosion films on machined uranium surfaces was made to ensure that no major threat to the integrity of uranium parts is introduced by the change of machining coolant from perchlorethylene and mineral oil to an aqueous solution of propylene glycol and borax.

Uranium coupons were machined with the "new" coolant, an aqueous solution of propylene glycol and borax, and with the "old" coolant, perchloroethylene and mineral oil, at machining speeds simulating typical production. The new coolant machined coupons were cleaned by two water rinses followed by two denatured alcohol rinses which were sprayed on and then wiped with a paper towel. The old coolant machined coupons were cleaned in perchloroethylene.

Positive secondary ion mass spectra can be compared using Figures 14A and 14B, old coolant machined, and Figures 15A and 15B, new coolant machined. In general, the surfaces are similar. The number and kind of contaminant elements are almost identical. Some differences in levels might be noted. The new coolant machined surface is a little higher in calcium (Ca), aluminum (Al), and silicon (Si), but the old coolant machined surface is higher in sodium (Na), potassium (K), and chlorine (Cl). The negative secondary ion mass spectra, which show the electronegative elements on the surface, can be compared using Figure 16, old coolant machined, and Figure 17, new coolant machined. The greatest difference appears to be in the greater Cl concentration on the surface of the old coolant machined surface. The new coolant surfaces are higher in carbon (C) containing residues (evidenced by peaks C, C_2, CN, CNH).

Secondary ion depth profiles were obtained to illustrate any differences in penetration or corrosion of the surfaces by the different coolants. Figure 18 shows $^{11}B^+$ depth profiles on both samples. Boron is several times more concentrated on the surface of the new coolant machined surface, but the profile shows that the contamination is at the surface only. In Figure 19, oxygen profiles are shown. The profiles show a thin oxide layer, ≤50nm thick, on the surface of each sample. The layer appears slightly thicker on the new coolant machined surface. Figure 20, ^{35}Cl depth profile, shows that Cl is more concentrated on the surface of the old coolant machined surface and extends through the oxide layer. On the new coolant surface, Cl is a surface contaminant only.

In summary, greater Cl contamination was found on the surface of the perchloroethylene mineral oil machined surfaces, but slightly greater oxidation was found on the surfaces machined with the new coolant. This greater oxidation is likely due to the increased water exposure since water accelerates the oxidation of uranium. However, this exposure can be minimized by cleaning with nonaqueous solvents after machining. Overall,

the differences on the machined surfaces are small and the change does not appear to constitute a significant threat to the integrity of machined uranium parts.

Future Work

No additional work is planned at this time. However, additional characterization of similar surfaces is expected for comparison purposes as coolant formulations, practices, and cleaning procedures are changed or standardized.

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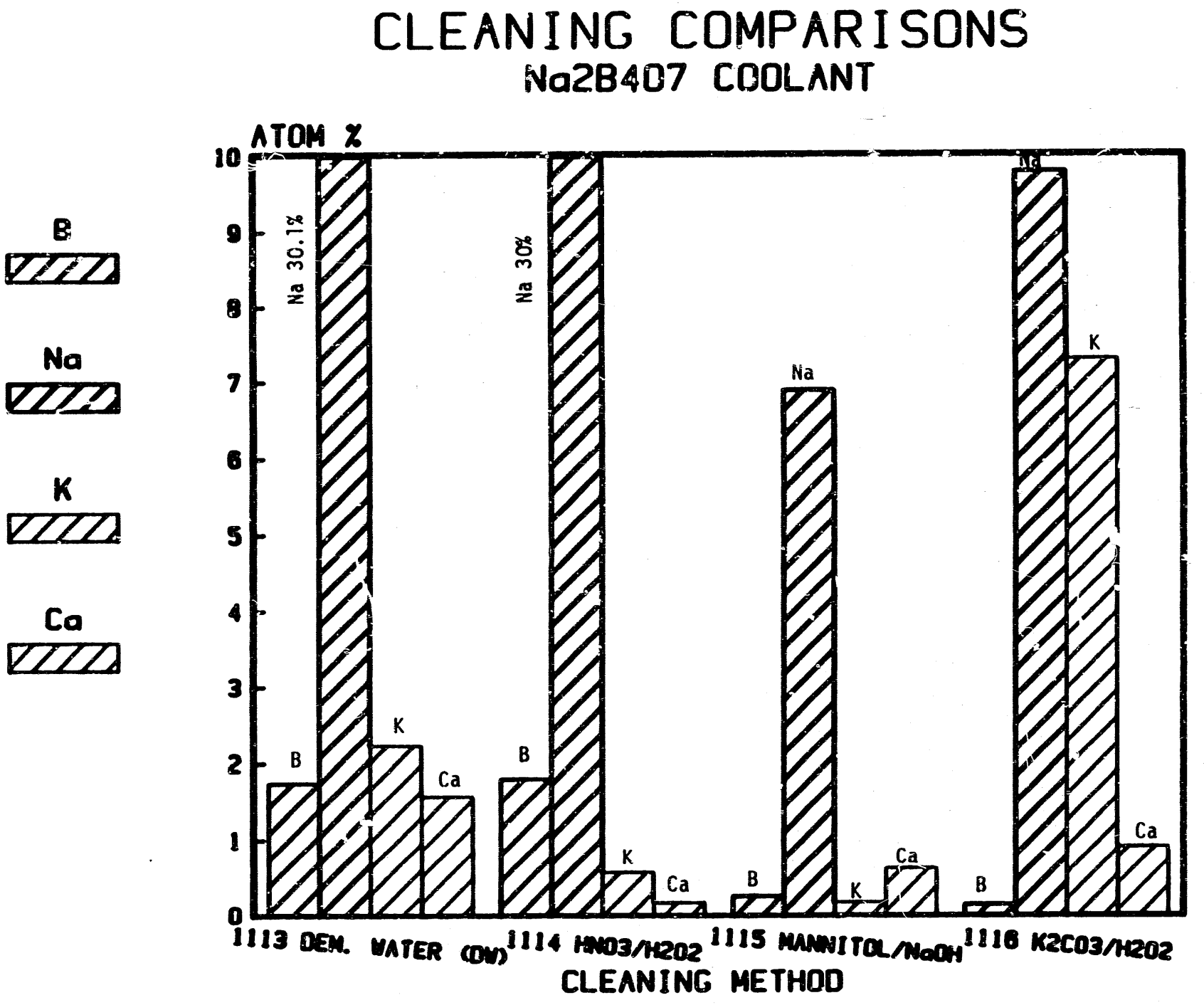
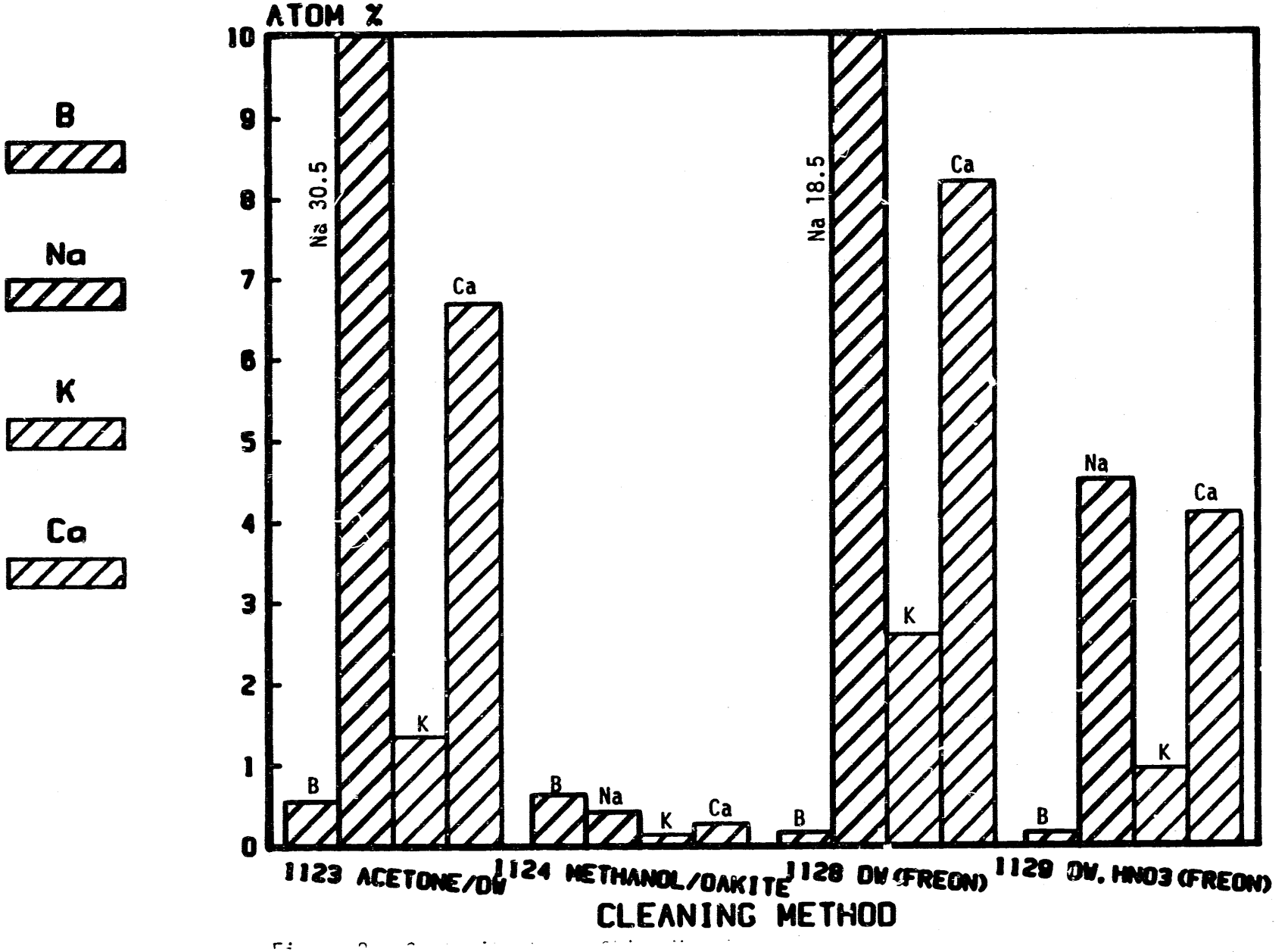
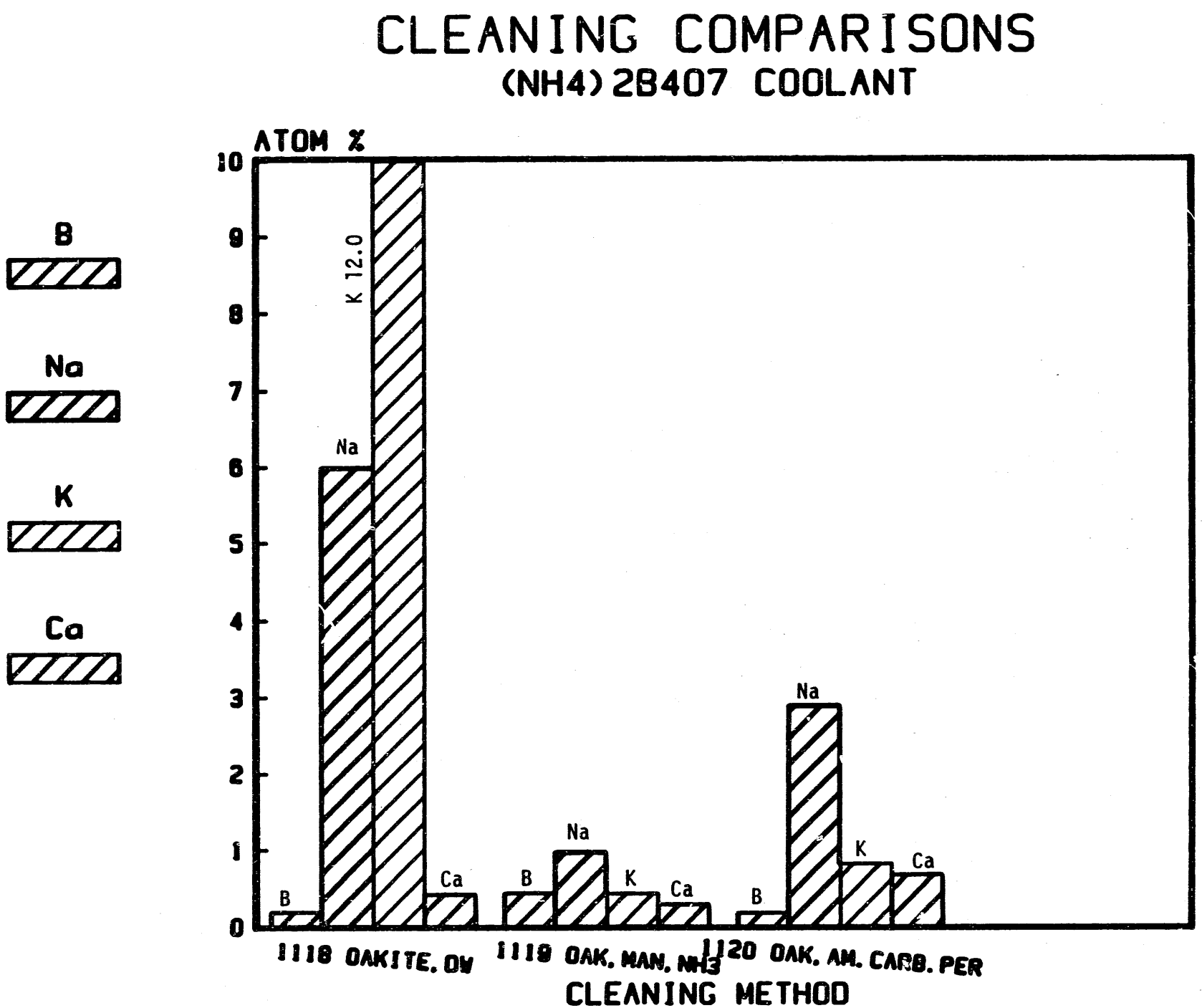


Figure 1 Contamination

CLEANING COMPARISONS

Na2B407 COOLANT




CLEANING COMPARISONS
(NH4)2B407 COOLANT
ATOM %
B
Na
K
Ca
10
9
8
7
6
5
4
3
2
1
0
K 12.0
Na
B
Ca
B
Na
K
Ca
B
Na
K
Ca
1118 OAKITE. OW
1119 OAK. MAN. NH3
1120 OAK. AM. CARB. PER
CLEANING METHOD

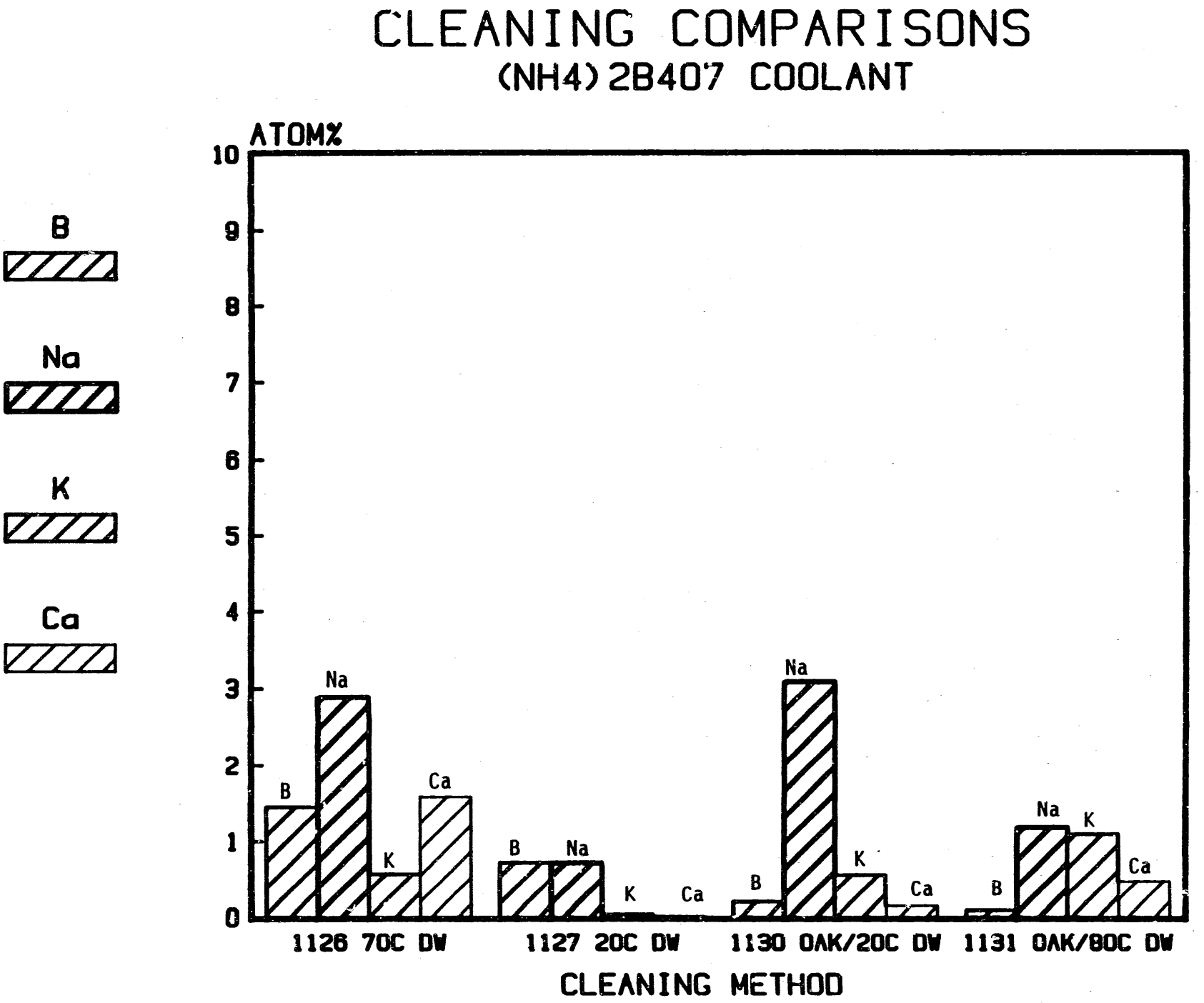


Figure 4 Contamination

CLEANING COMPARISONS
TEA-B407 COOLANT

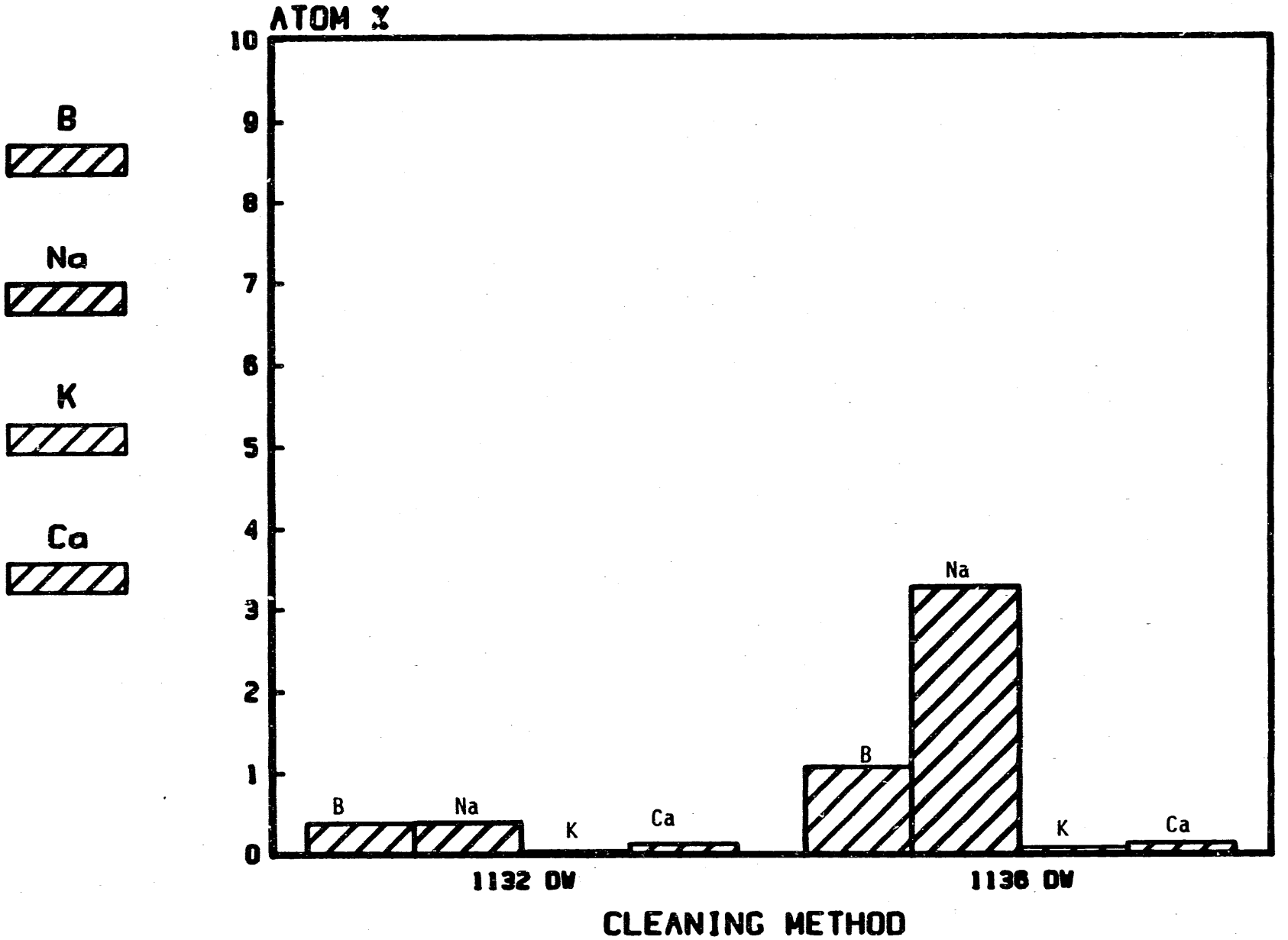


Figure 6. Boron on 1113. Ultrasonically Cleaned in Demineralized Water.

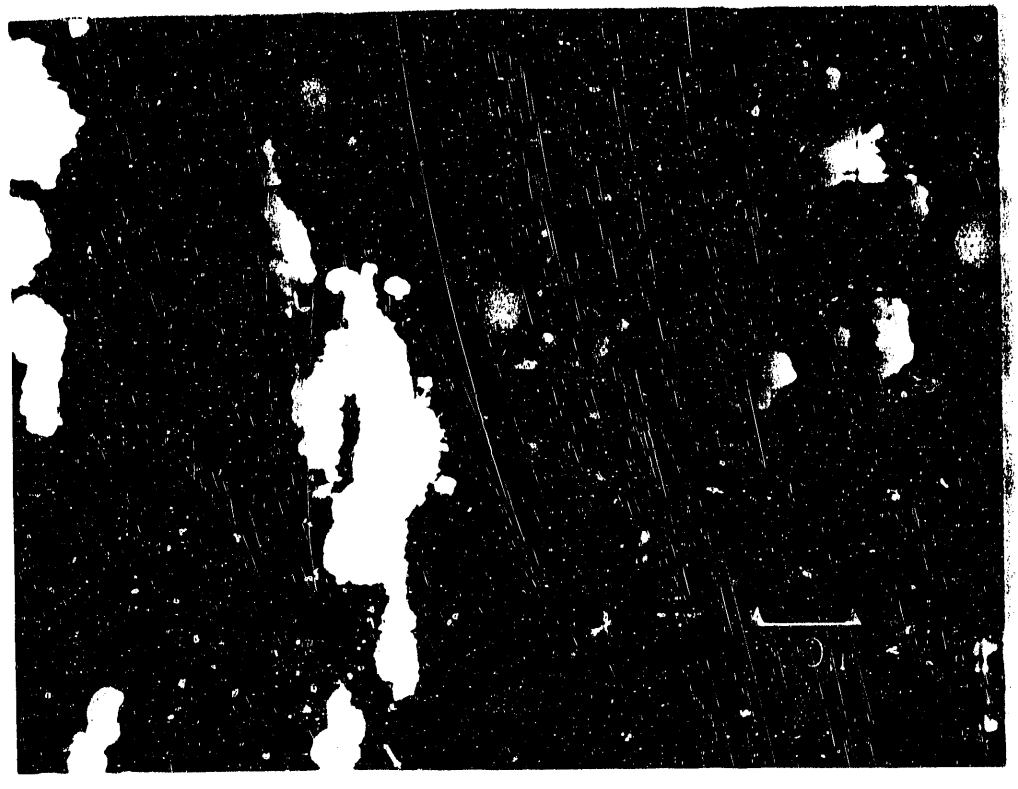


Figure 7. Sodium on 1113. Same Area as Figure 6.

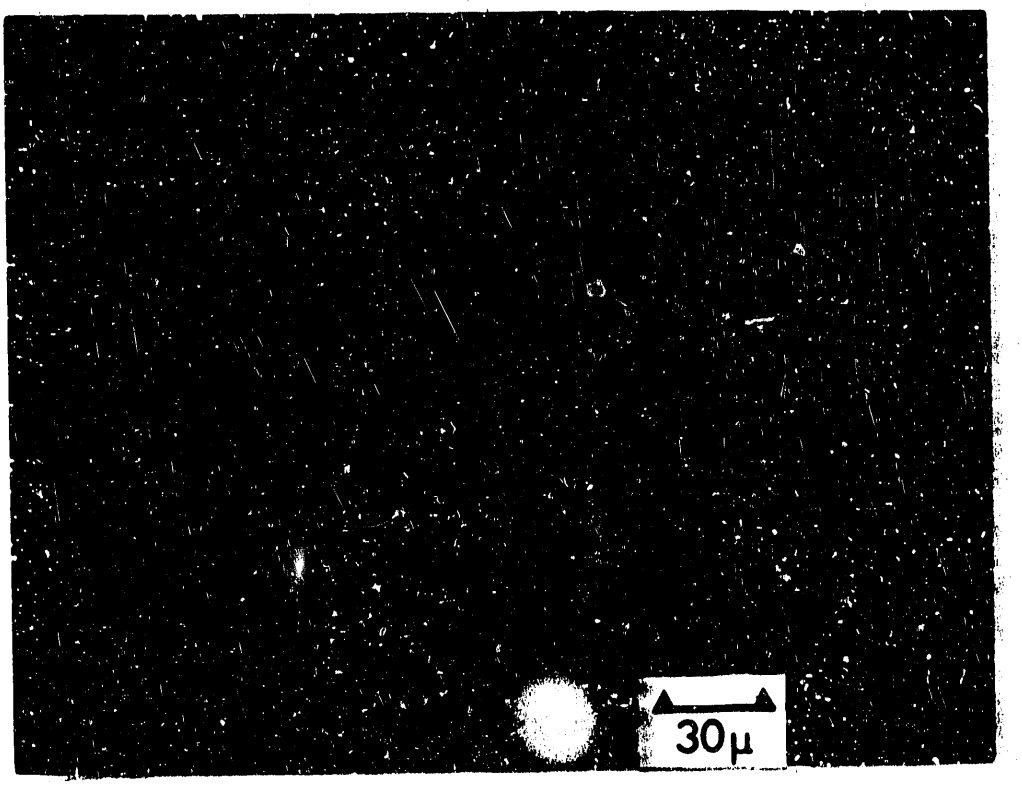


Figure 8. Boron on 1116. Ultrasonically Cleaned in 5% K_2CO_3/1% H_2O_2

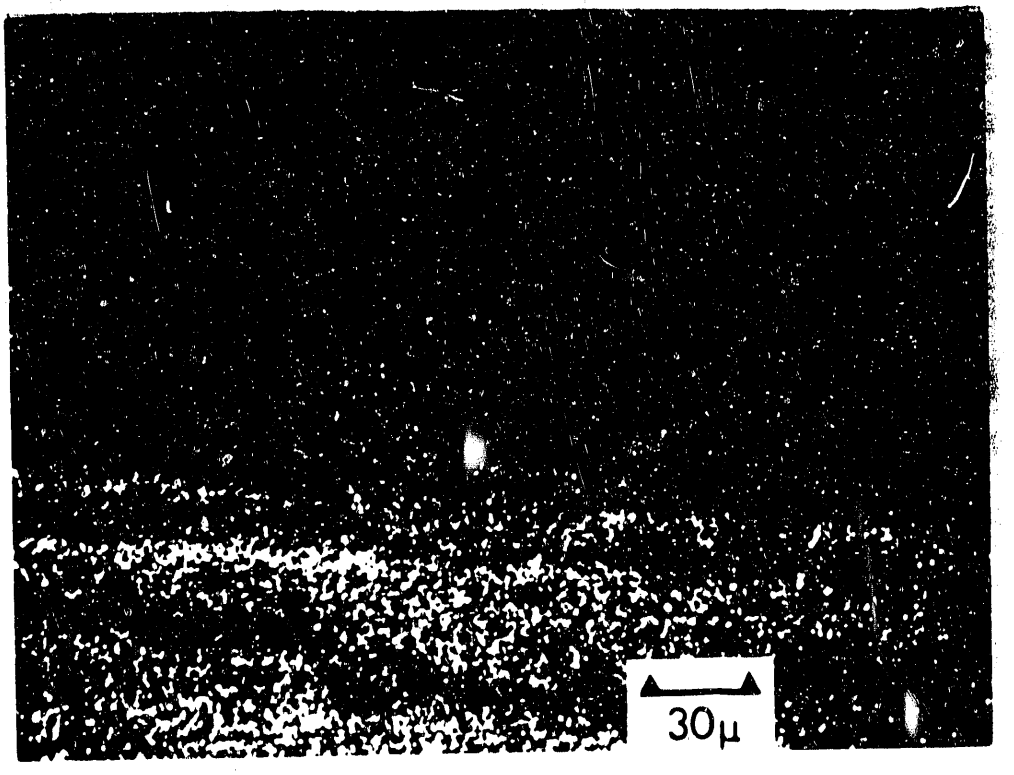
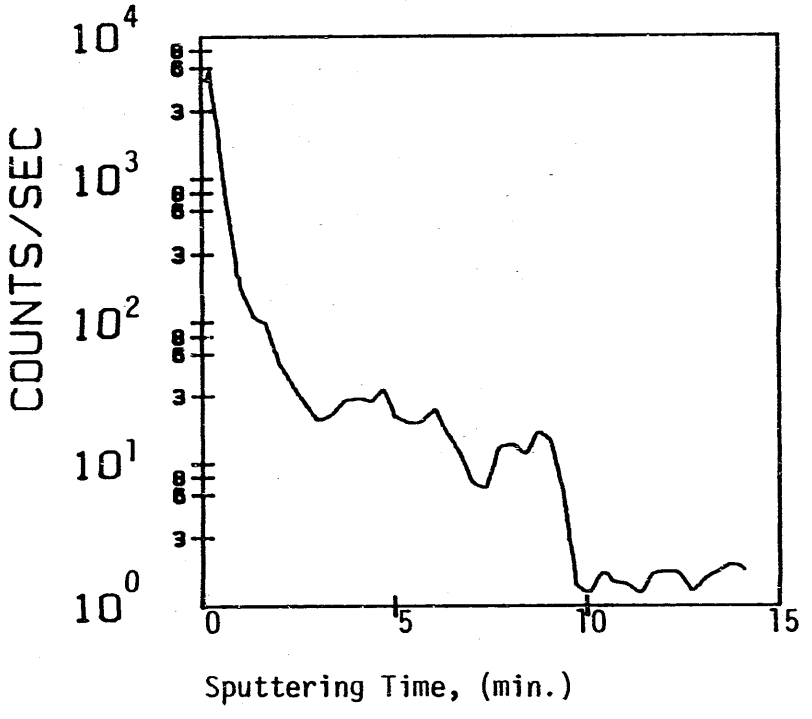
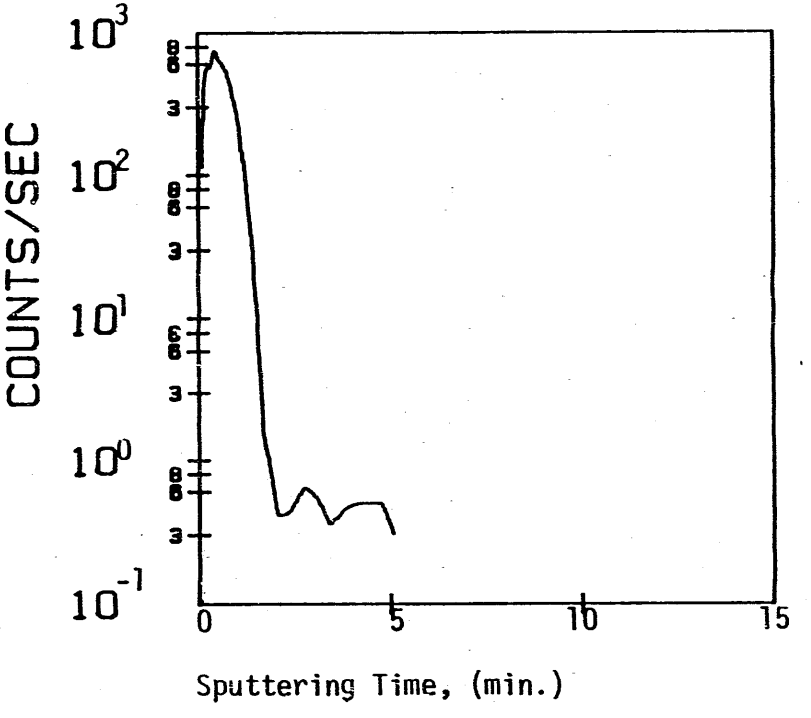


Figure 9. Sodium on 1116. Same Area as Figure 8.



A. From Small Boron-Containing Island in Upper Right of Figure 6.



B. From Area Between Boron-Containing Islands

Figure 10. Depth Profiles of Boron on Sample 1113.

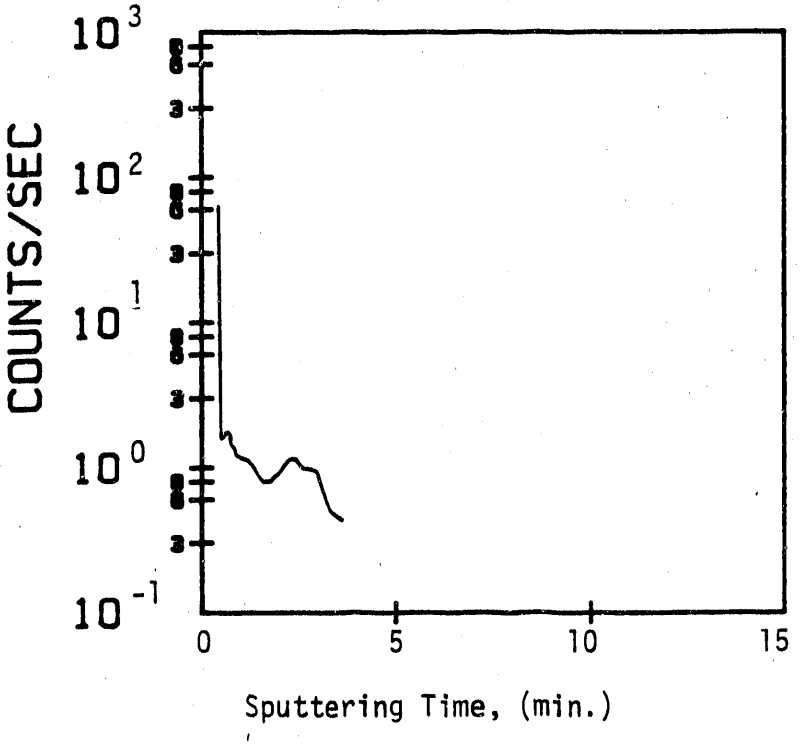


Figure 11. Boron Porfile on Sample 1128, Typical of Samples with Low Boron.

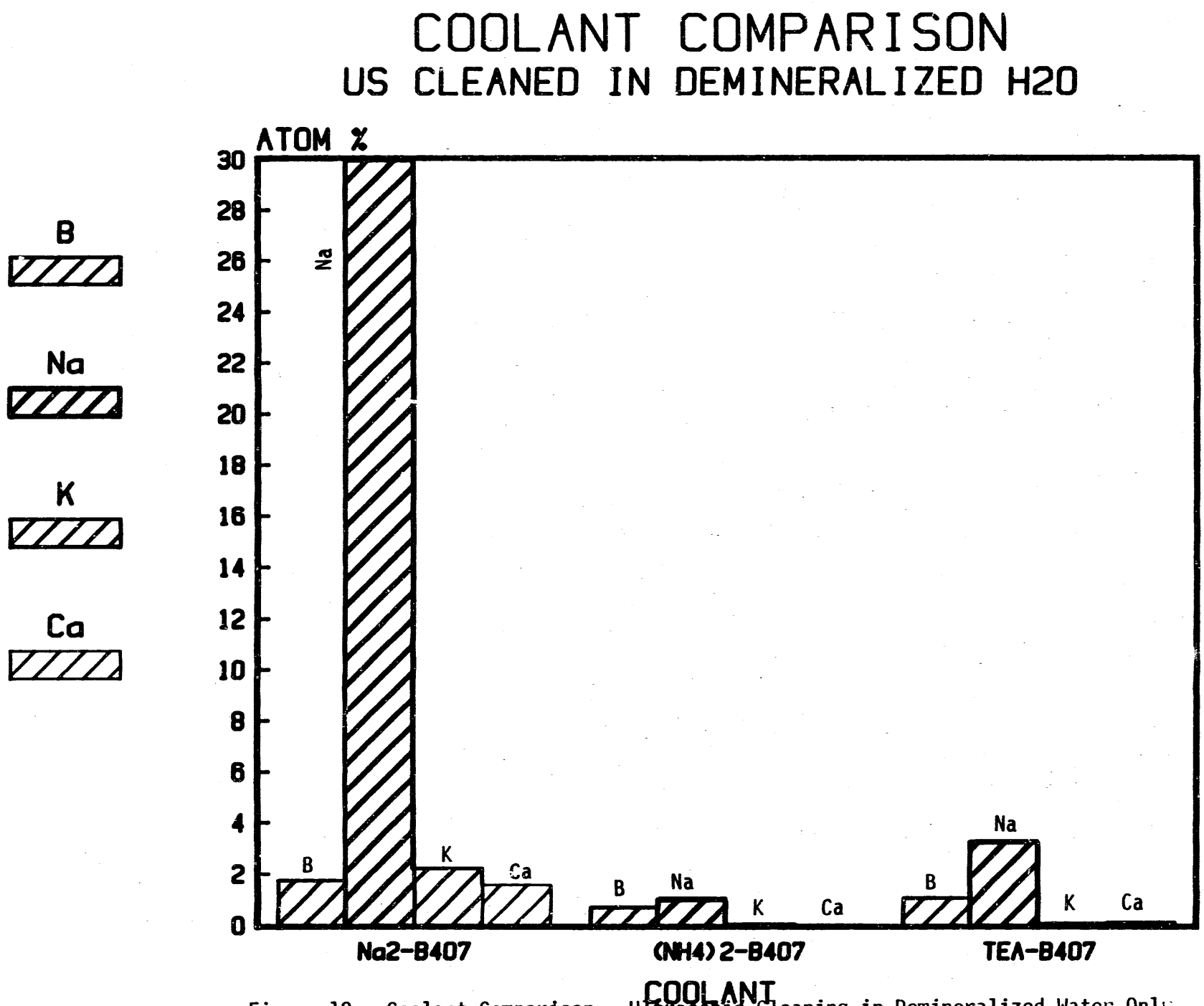


Figure 12. Coolant Comparison - Ultrasonic Cleaning in Demineralized Water Only

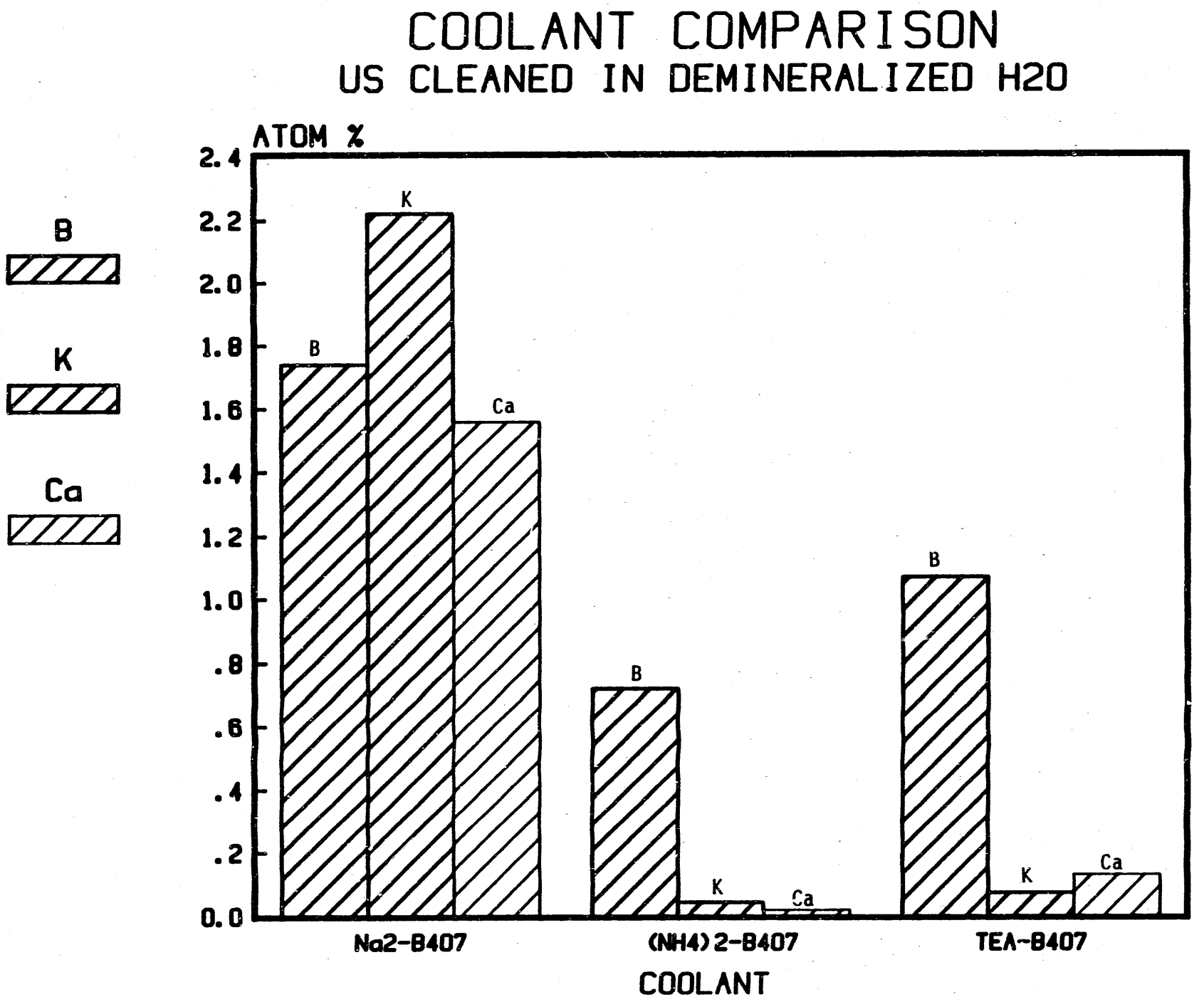


Figure 13. Coolant Comparison--Ultrasonic Cleaning in Demineralized Water Solution

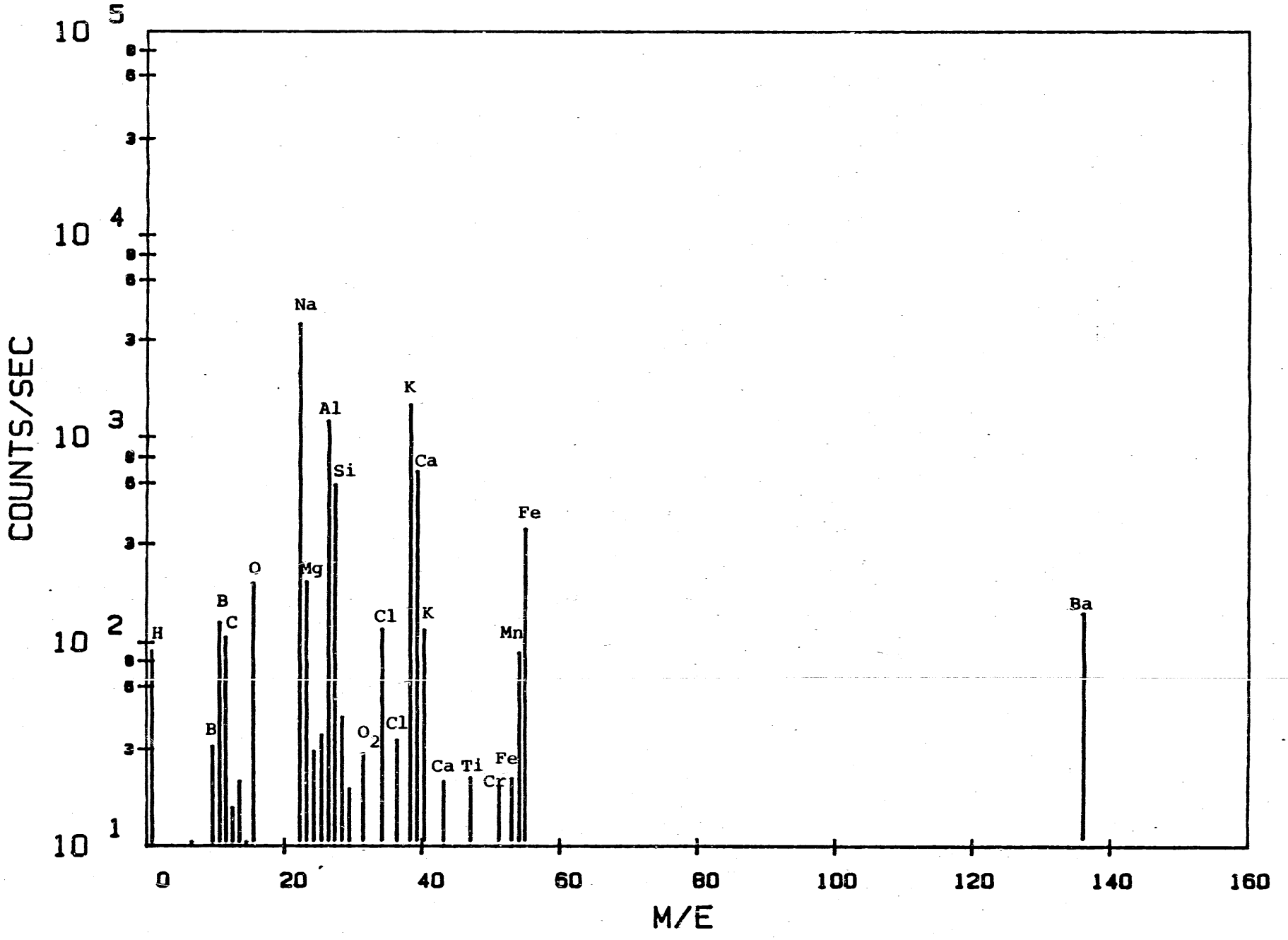


FIGURE 14A. Positive Secondary Ion Mass Spectrum of Old Coolant Machined Uranium, m/e = 0-160

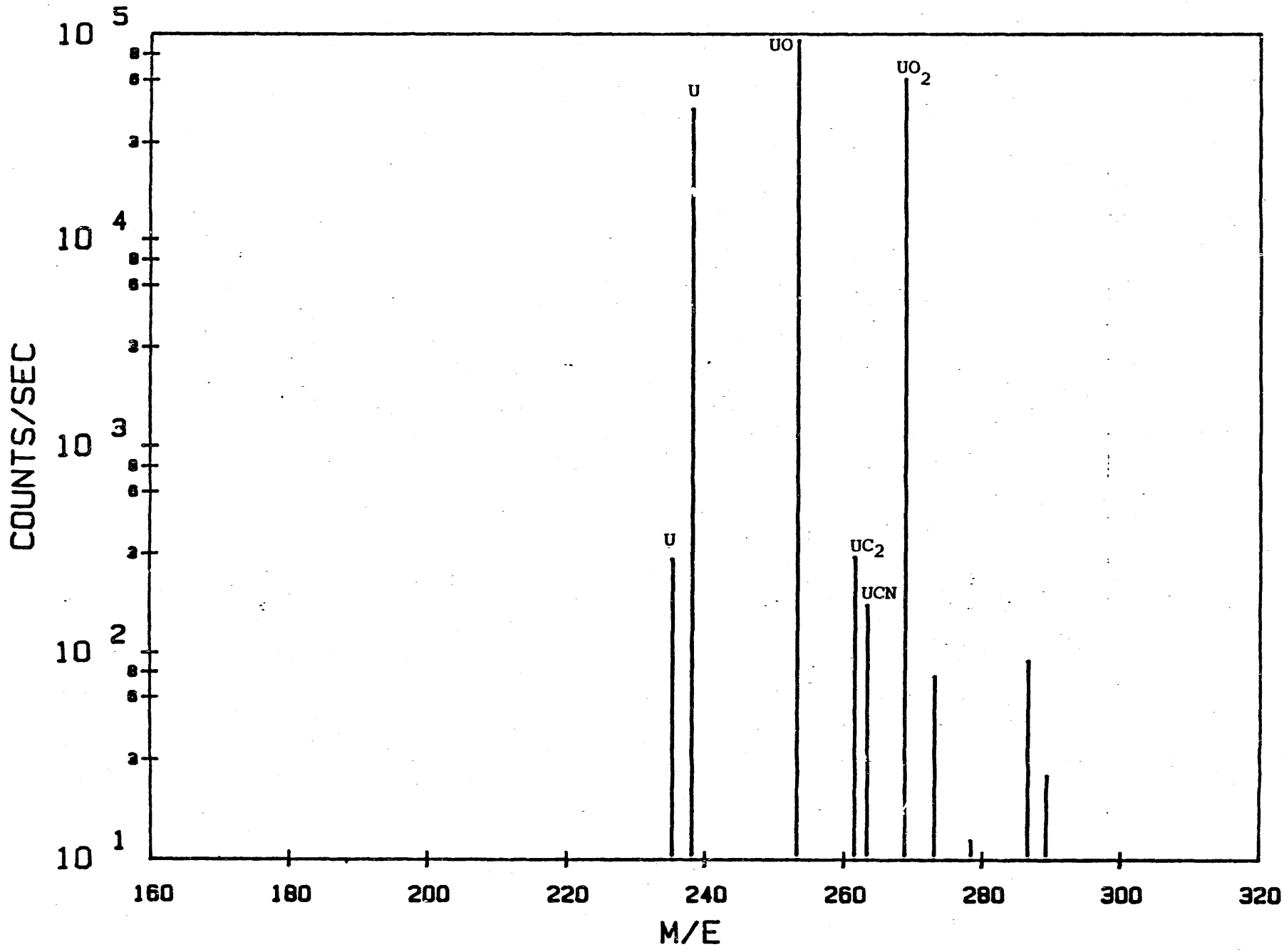


FIGURE 14B Positive Secondary Ion Mass Spectrum of Old Coolant Machined Uranium, m/e = 160-320

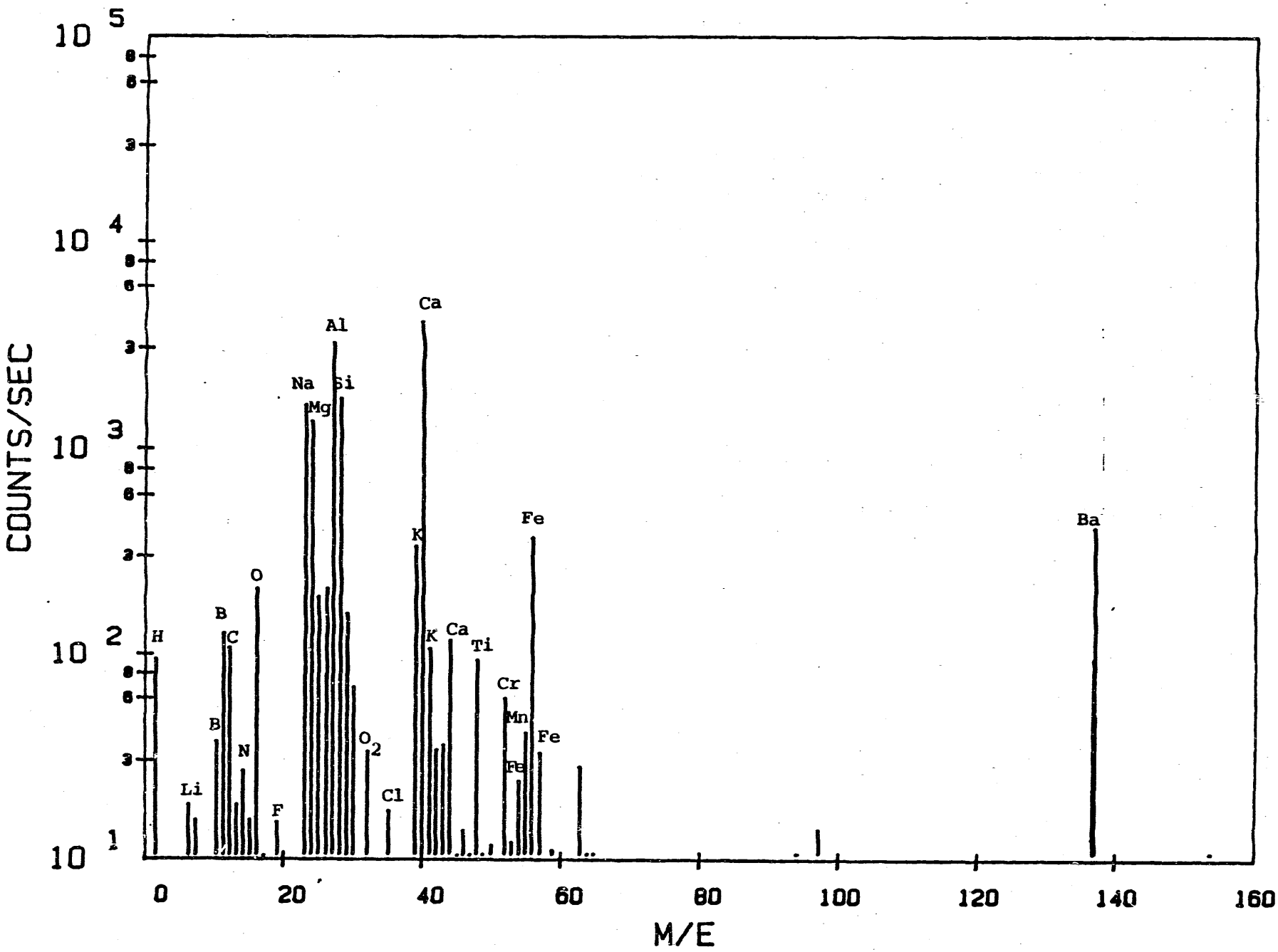


FIGURE 15A Positive Secondary Ion Mass Spectrum of New Coolant Machined U, m/e = 0-160

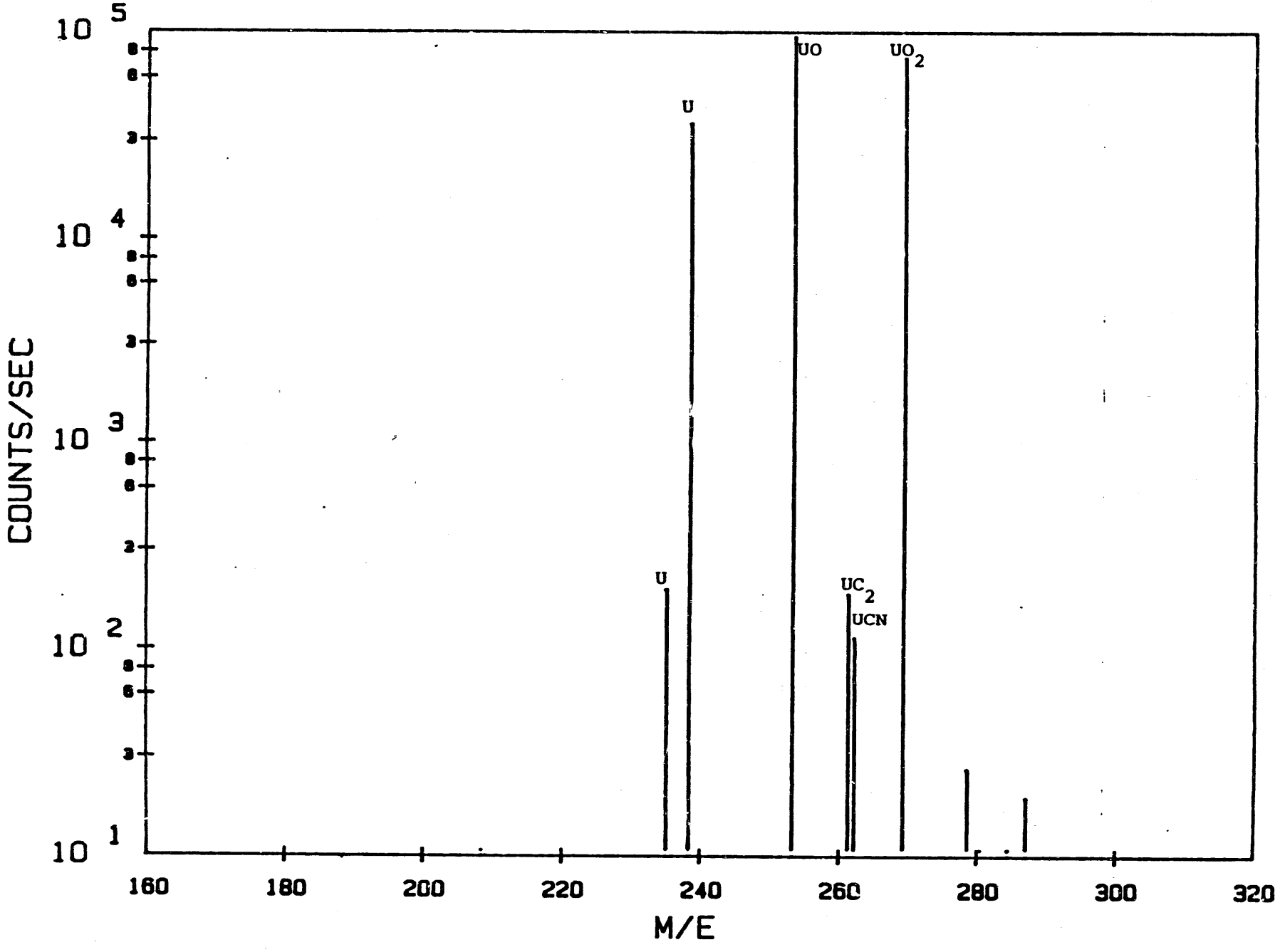


FIGURE 15B Positive Secondary Ion Mass Spectrum of New Coolant Machined Uranium, m/e = 160-320

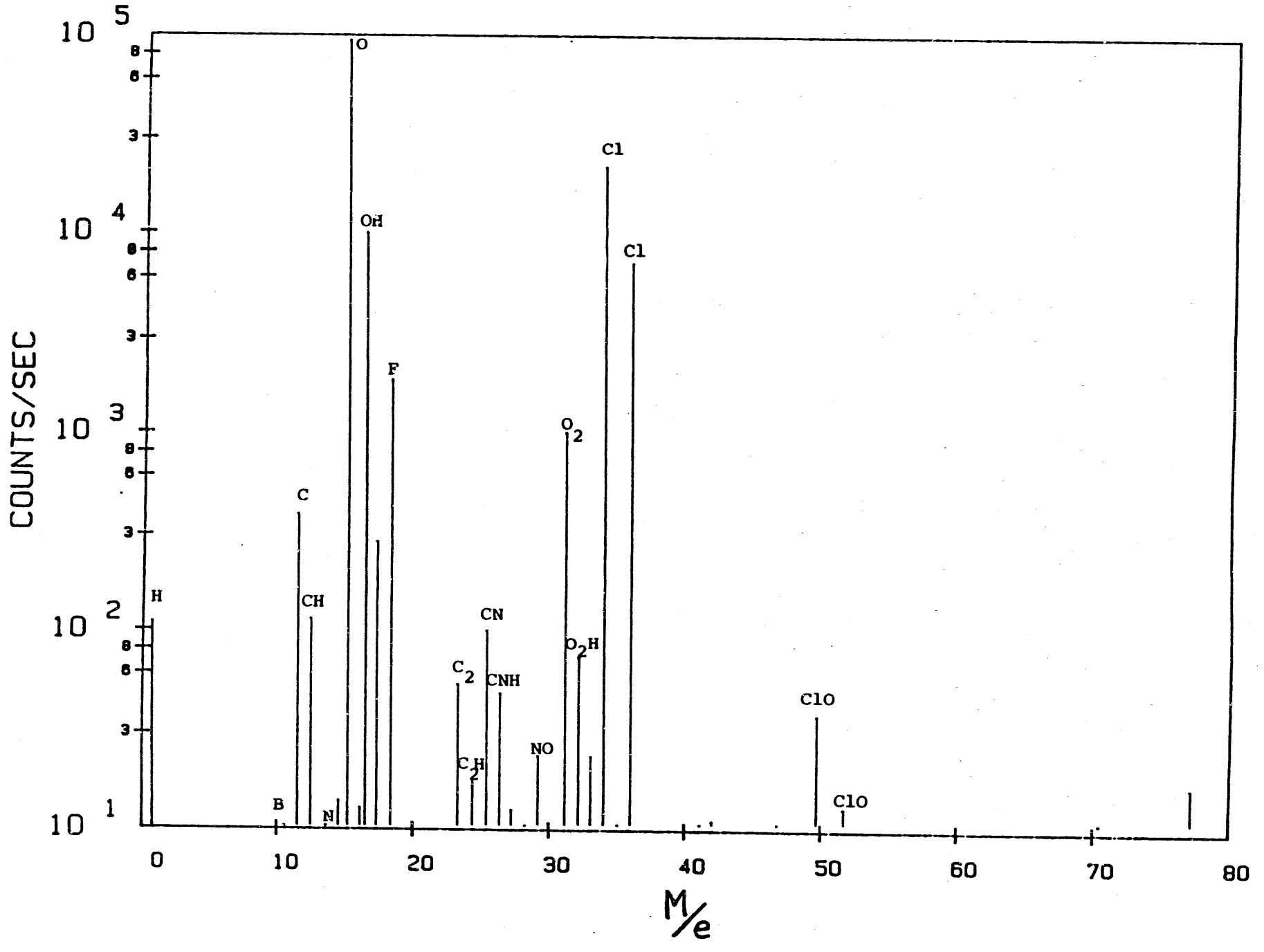


FIGURE 16 Negative Secondary Ion Mass Spectrum of Old Coolant Machined Uranium

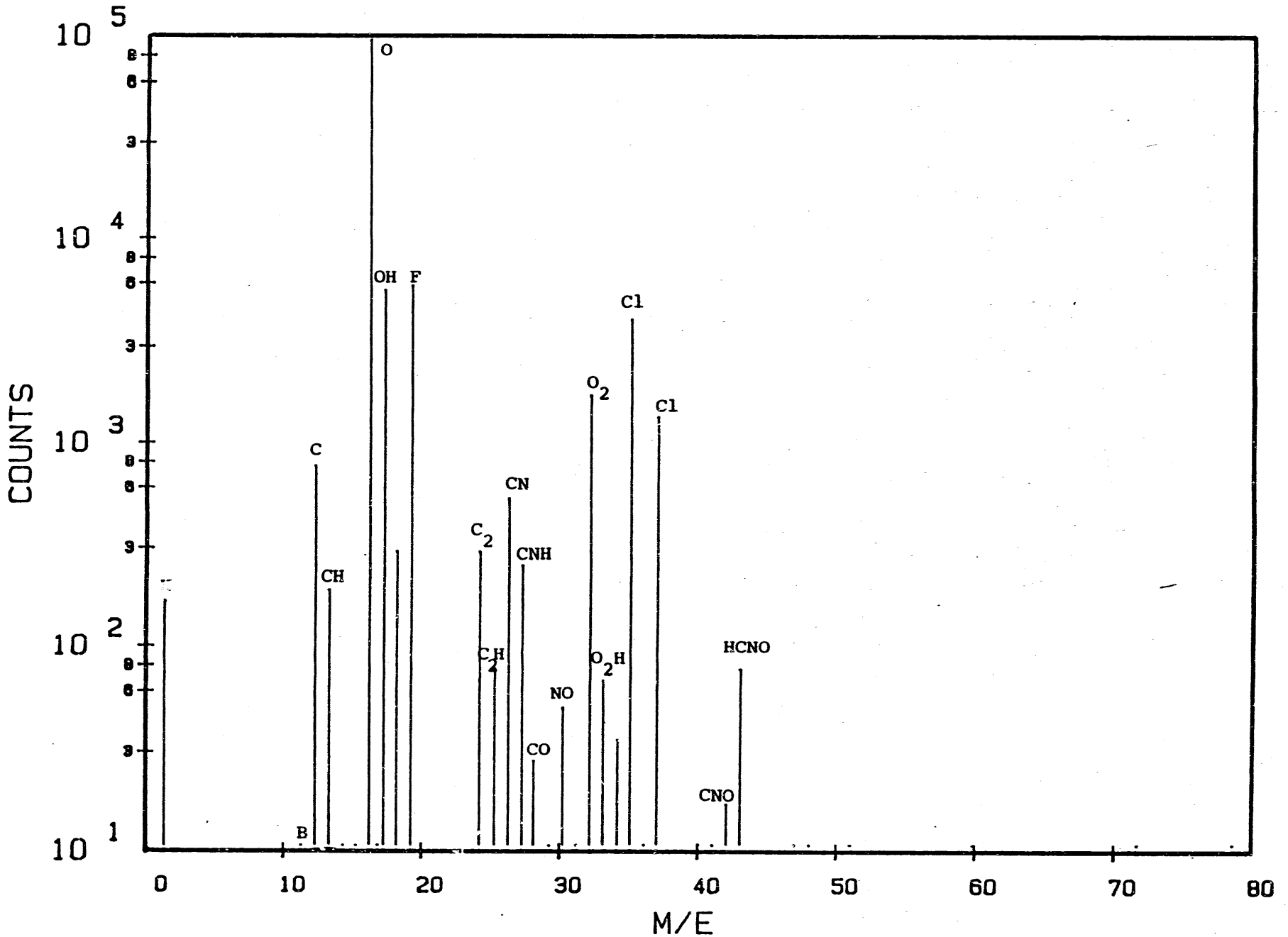


FIGURE 17 Negative Secondary Ion Mass Spectrum of New Coolant Machined Uranium

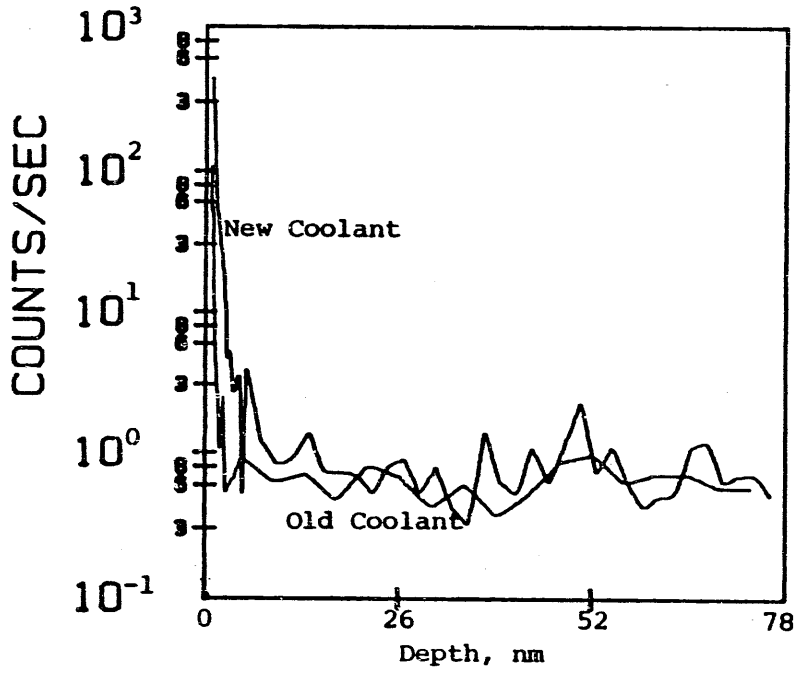


FIGURE 18 Boron Secondary Ion Depth Profiles ($^{11}B+$)

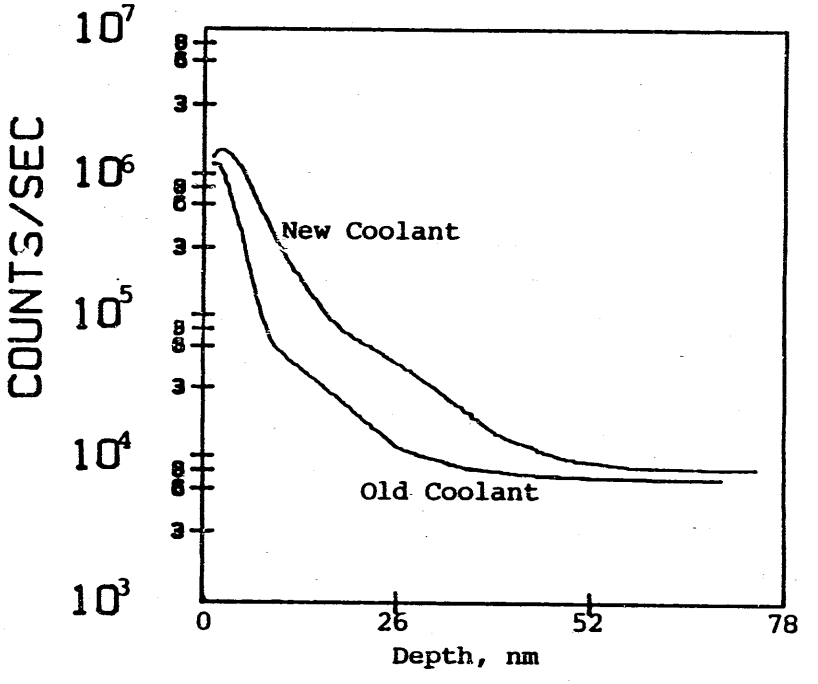


FIGURE 19 Oxygen Secondary Ion Depth Profiles ($^{16}O-$)

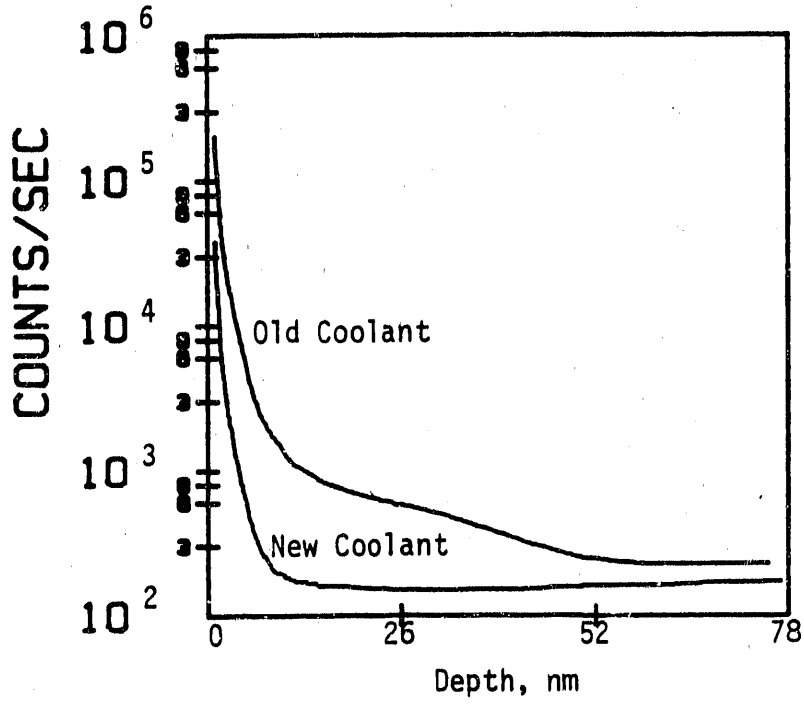


Figure 20. Chlorine Secondary Ion Depth Profiles ($^{35}Cl^{-}$)

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