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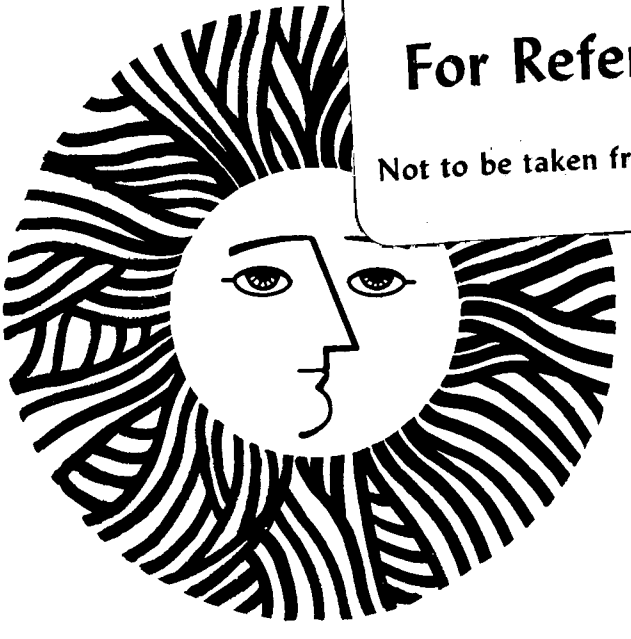

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LAWRENCE BERKELEY LABORATORY
Room: 128 Bldg.: 70 Ext.: 6698

December 4, 1979

TO: Art Hartstein

FROM: Phyllis Fox, Richard Fish, and Mathilde Kland

RE: November Monthly Progress Report
The Partitioning of Major, Minor and Trace Elements during Simulated In Situ Oil Shale Retorting
LBID-145

Navy Core Project

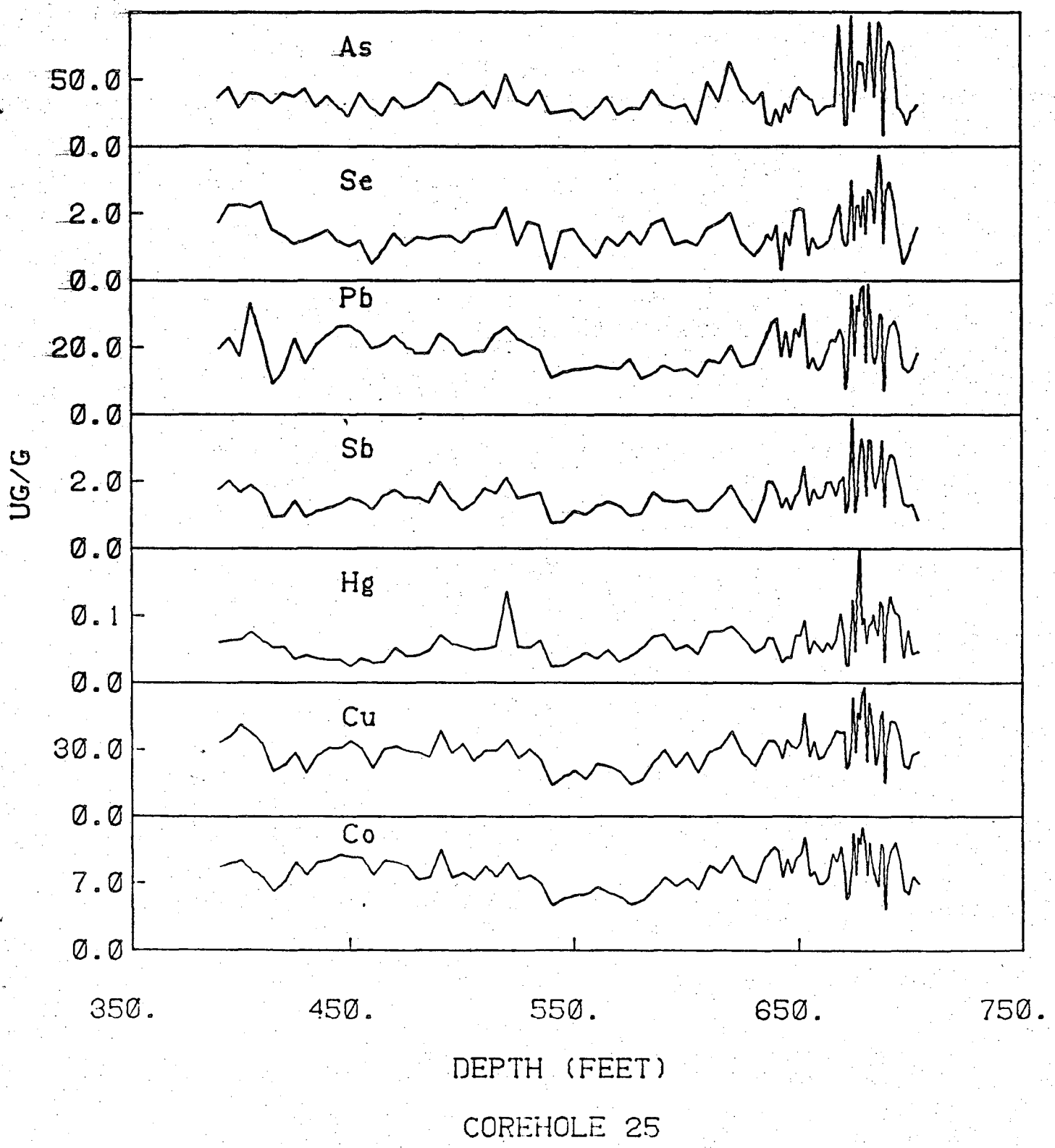
The statistical techniques developed previously were used to analyze the mineralogical, elemental, and Fischer Assay data from corehole 25 on the Naval Oil Shale Reserve. The results of these analyses were presented in a seminar at LETC on November 30. These analyses revealed that the ratio of the maximum to the minimum observed concentration ranged from 2 to 4 for all elements except Na, K, As, Se, Mo, Cu and Pb. The weight percent water correlated very strongly with analcime and illite. The variation in the chacophile elements As, Se, Pb, Sb, Hg, Cu, and Co as a function of depth in the formation is shown in Figure 1.

Mass Balance Studies

Thermodynamic calculations were initiated to predict the volatility of elements during oil shale retorting and to identify stable gas phase species. The retort was divided into combustion, pyrolysis, preheat, and discharge zones and chemical equations written describing metal reactions likely to occur in each zone. Thermodynamic constants were then used to determine equilibrium constants and these were used to compute species distributions. These calculations were completed for Hg and suggest that elemental mercury is formed in the pyrolysis zone by reduction of HgS by H_2 and CO and by direct decomposition of HgS and in the combustion zone, by oxidization of HgS. Once the mercury is released,

Figure 1

Vertical variation in As, Se, Pb, Sb, Hg, Cu, and Co in core 25 from the Naval Oil Shale Reserve



it may be recondensed as HgO at temperatures below 300°C. The stable gas phase species are Hg, HgO(g), $Hg(CH_3)$, $Hg(CH_3)_2$, and Hg_2. Elemental mercury is the stable and predominant specie in all four retort zones. Methyl and dimethyl mercury may form in the preheat and discharge zones but they are thermodynamically unstable in the combustion and pyrolysis zones. These predicitions are consistent with measurements.

Experiments were continued to identify and quantify the mechanisms responsible for the partitioning of trace elements to MIS retort water. Weighted quantities of raw shale and shale oils were contacted separately with NH_4HCO_3 solution and the filtrate analyzed by XRF and ICP. Preliminary results of these experiments indicate that the As, Se, and B in retort waters originate from leaching of raw shale and oil in the cool zone ahead of the reaction front.

β-Diketone - Metal Complexes

Our recent use of β-diketone ligands to extract organometallic and inorganic compounds from retort waters has been expanded. We initiated our studies with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD) and now have also used di-pivaloylmethane (HDPM).

We have concentrated on being able to gas chromatograph (capillary column) the β-diketone metal complexes of HFOD and HDPM with Zn, Ni, Hg, Cu, and Al as representative metals. The authentic samples $(DPM)_2Zn$, $(DPM)_2Hg$, $(DPM)_2Cu$, $(DPM)_2Ni$, $(FOD)_2Zn$, $(FOD)_2Hg$, $(FOD)_2Cu$, $(FOD)_2Ni$, and $(FOD)_3Al$ were analyzed by capillary gas chromatography-electron impact mass spectrometry (GC-EIMS). Figures 2 and 3 show representative electron-impact mass spectra.

Presently, we are pursuing research designed to optimize the extraction of Se, Zn, Hg, and Cu from aqueous solution in order to verify the use of β-diketones as suitable ligands for the ultimate analysis of these metals in retort waters by GC-EIMS and GC-CIMS.

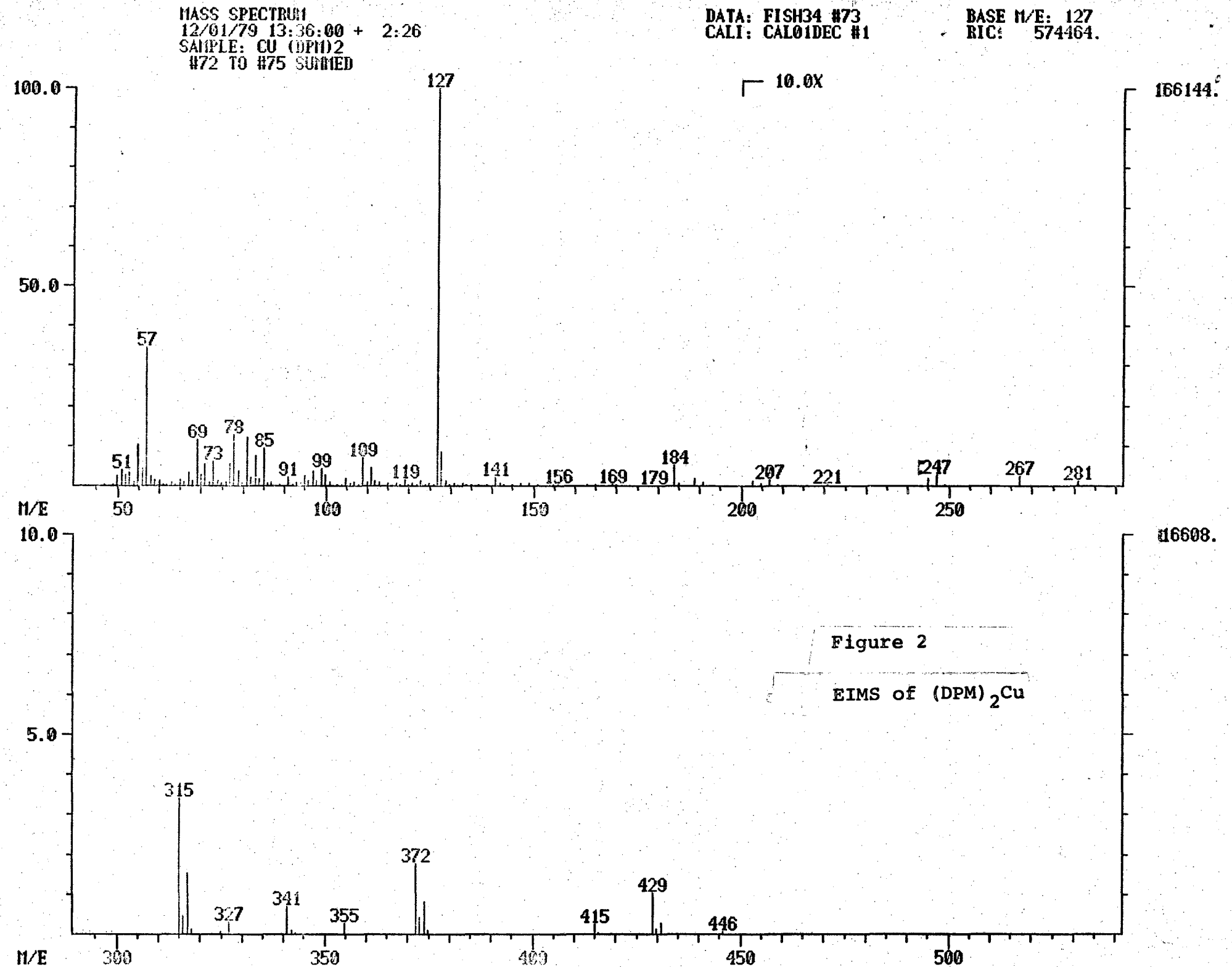


Figure 2

EIMS of $(DPM)_2Cu$

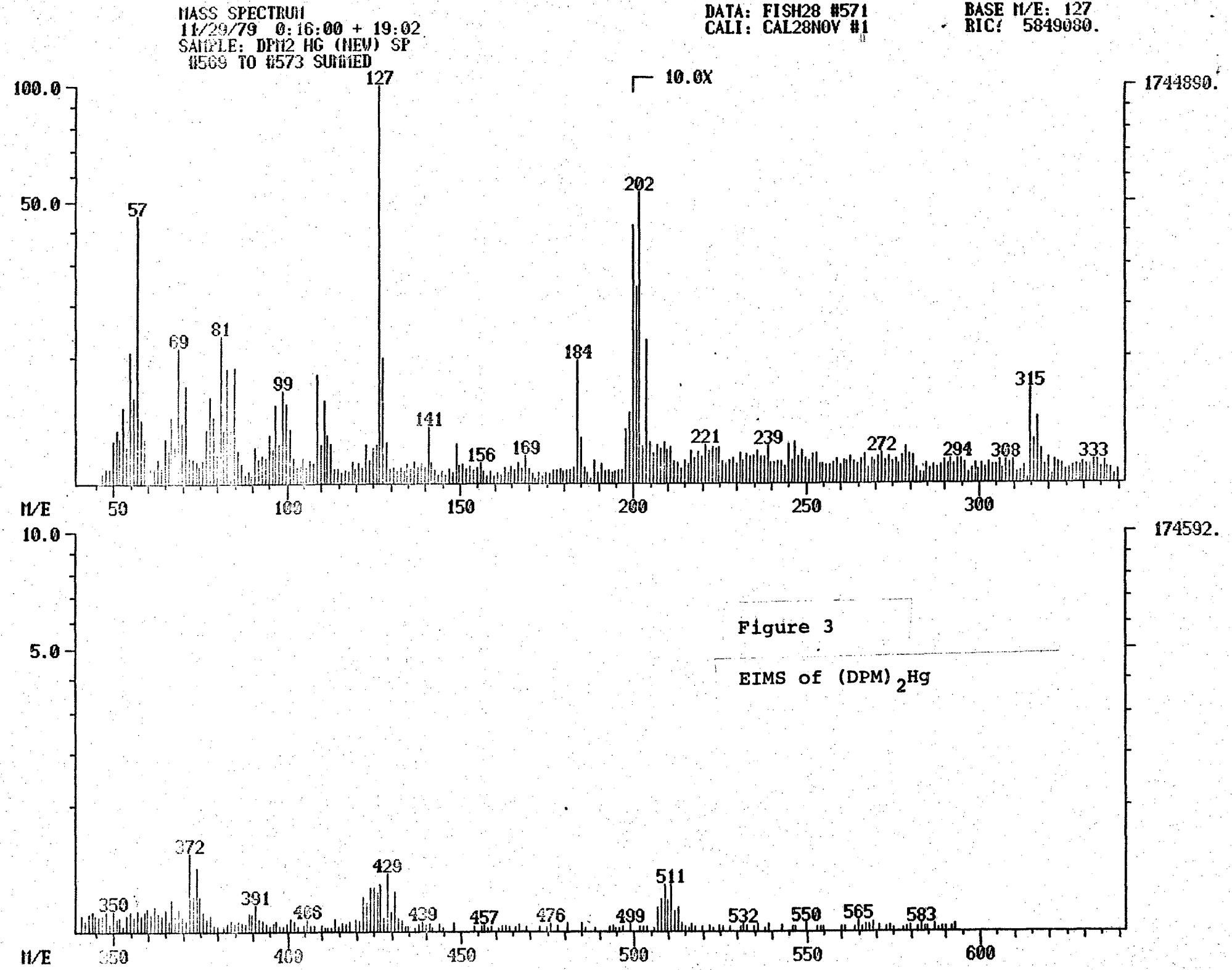


Figure 3

EIMS of $(DPM)_2Hg$

Organoarsenic and Inorganic Arsenic Speciation by High Performance Liquid Chromatography using Graphite Furnace Atomic Absorption Detection

Eight oil shale wastewaters were prepared by filtration and plans are underway to analyze these samples by high performance liquid chromatography in combination with graphite furnace atomic absorption detection. A collaborative effort in these speciation studies will be conducted with a group of colleagues at the National Bureau of Standards under the direction of Dr. Fred Brinckman. It is hoped that this method will allow, for the first time, identification of these potential health hazards in oil shale wastewaters and shale oils.

Identification and Quantification of Fatty Acids as Ligands of Metals in Oil Shale Waters

We have initiated a project to identify potential ligands of metals in oil shale wastewaters. One group of compounds, the fatty acids, are present in high concentrations in retort waters, but analysis of these potential ligands has been limited. Thus, we have taken five oil shale wastewaters--150-ton retort water, Oxy boiler blowdown, Oxy product water, Oxy heater treater water and LLL retort water L-3--and lyophilized 20 ml samples.

Since the methyl esters of these fatty acids are easier to analyze, we methylated the freeze dried residues with boron trifluoride in methanol. Analysis by capillary gas chromatography with authentic samples allowed us to tentatively identify C_6 to C_{15} fatty acids. Unequivocal confirmation of these compounds will be carried out by capillary gas chromatography in combination with chemical ionization mass spectrometry and the results reported in the future.

X-ray Flourescence Analysis of Metals in Organic Extracts using a Cellulose Pellet Technique

A new method was developed to analyze metals in methylene chloride extracts. Previously, seven 4-µl drops of organic extract were pipetted in a symmetrical pattern onto a 0.006 mm polypropylene film, vacuum dried, and analyzed on a high-energy, energy-dispersive x-ray fluorescence spectrometer. In this procedure, it was necessary to use a 1:1 solution of ethanol/water to dissolve the internal standard. This led to erratic results, presumably due to the much lower surface tension of ethanol/water which caused unsymmetrical drop deposition. In the new technique, microcrystalline cellulose is slurried with the CH_2Cl_2 extract, and the solvent is evaporated to dryness with stirring at room temperature. The resulting dry powder is pressed into a pellet and analyzed as previously. The results of analyses of a CH_2Cl_2 extract of 150-ton retort water and a phenyl arsonic acid standard (10 ppm) are shown in Table 1. The reproducibility is satisfactory and the results obtained on the phenyl arsonic standard are accurate.

Table 1

XRF Analysis of a CH_2Cl_2 Extract of 150-ton Retort Water using the Cellulose Pellet Technique

	150-ton CH_2Cl_2 Extract[a,b] ppm (orig. sample)	10 ppm as Standard[c] ppm (orig. sample)
Fe	7.4 ± 0.8	0.24 ± 0.07
Ni	2.0 ± 0.4	0.10 ± 0.04
Cu	2.5 ± 0.4	0.43 ± 0.04
Zn	1.9 ± 0.3	0.23 ± 0.03
As	2.2 ± 0.2	10.4 ± 1.0
Se	3.2 ± 0.3	<0.10
Br	3.8 ± 0.4	0.11 ± 0.03

[a] ppm x 5

[b] 0.35 ml sample/1.65 ml CH_2Cl_2/350 mg cellulose

[c] 2.00 ml standard solution/150 mg cellulose

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