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THE OIL CONTENT OF SEDIMENTS
IN THE SUMP OF A SALT DOME SOLUTION-MINED CAVERN
USED FOR CRUDE OIL STORAGE

Final Report

by -

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1.0 INTRODUCTION

In the United States, the Energy Policy and Conservation Act of 1975 established the requirement for a Strategic Petroleum Reserve (SPR) of up to one billion (10^9) barrels of oil. The Federal Energy Administration, now a part of the Department of Energy (DOE), was tasked with implementing the SPR. The majority of the oil comprising the SPR will be stored in solution-mined caverns in salt and in conventionally dry-mined chambers in salt and in other rocks.

Until recently there was little information available on the effects of long-term storage on the quality of crude oil and distillate fuel oil. Detailed studies performed by Kavernen Bau- und Betriebs-GmbH (KBB GmbH), under contract to DOE, demonstrated that crude oil and distillate fuel oil stored in solution-mined caverns in salt will not undergo any deleterious changes in quality.

Following completion of these earlier studies by KBB GmbH, a contract between DOE and PB-KBB, Inc. was executed to:

- o Evaluate the effects of long-term storage in a potash mine on the physical and chemical properties of crude oil; and
- o Determine the oil content of the sediments in the sump of a salt dome solution-mined cavern used for crude oil storage.

This report details the results of the latter study.

Petroleum hydrocarbons, through one of several mechanisms, could conceivably accumulate in the sump sediment of a salt dome solution-mined cavern used for crude oil storage. The most likely mechanism would involve the adsorption of an oil film onto the sediment particles inherently present in crude oil; or suspended in the surface water used to leach the cavern, periodically displace increments of the stored crude oil, or to flush the oil-filled brine string following workover operations. A second mechanism would involve the settling out of heavy asphaltic compounds; while a third mechanism would be as fluid inclusions in salt crystals which formed at the oil/brine interface. The sediment particles would electrolytically flocculate, while the asphaltic compounds and salt crystals, because of their greater density relative to brine, would eventually settle to the sump.

If hydrocarbons were to accumulate in the sump sediment, they could become resuspended during later fluid transfers as a result of turbulence at the brine/sediment interface.

If displaced to the surface, these hydrocarbons could pose an environmental impact.

This report describes sediment sampling from the sump of a solution-mined cavern, analysis of the sediment, and an interpretation of the results.

The cavern the sump samples were taken from is one of 33 leached in the Etzel salt dome, near Wilhelmshaven, West Germany, and used for the storage of crude oil. Each of these caverns is designed for an initial capacity of 500,000 cubic meters (3.14×10^6 US bbl).

Through a turnkey contract awarded in 1971 by Industrieverwaltungsgesellschaft mbH (IVG) of Bonn, KBB GmbH of Hannover, West Germany, designed and constructed the Etzel cavern project. Although no longer involved in the development of Etzel, KBB GmbH, as a subcontractor to PB-KBB, Inc., was permitted to collect samples of sediment from the sump of cavern K 117 on November 28, 1979. Chemical and other analyses of these samples were carried out during December 1979 and January 1980.

2.0 SUMMARY

The studies reported herein were conducted to ascertain if petroleum hydrocarbons are likely to accumulate in the sump sediments of a salt dome solution cavern used for crude oil storage and, if so, which hydrocarbons and in what concentrations.

Cavern K 117 at Etzel was selected for sampling because considerable data were available pertaining to the cavern and its crude oil inventory as a result of earlier studies (KBB, Inc., 1979). Three samples were collected from the sump using a specially constructed device similar to corers used for obtaining samples of unconsolidated lacustrine and marine sediments.

Subsequent mineralogical analyses of these samples revealed that they predominantly consist of uncemented halite crystals, ranging up to several centimeters in length, with subordinate anhydrite, and traces of gypsum and clay. Some of the mineral particles are colorless and translucent, while others are noticeably contaminated with oil. The samples exuded a distinct petroleum odor.

Gas chromatographic analysis of an evolved gas sample showed the presence of the normal-paraffins propane (C_3) through octane (C_8). Gas chromatographic analyses of a solvent extract of the sediment showed hydrocarbon and sulfur-compound distributions typical of crude oil. An infrared spectrum of the extract was also characteristic of a weathered or topped crude oil. The hydrocarbon content of the sediment samples was determined to be 780 ppm on the basis of a tetrachloromethane extract.

It is believed that the petroleum present in the sump sediments principally results from cavern workover operations involving the pulling and resetting of the brine tubing string. When the brine string is reset it fills with oil because a packer is not used. To displace this oil, river water is pumped down the tubing at a moderately high rate. During this flushing process, clay particles dispersed in the river water adsorb a film of oil. As the oil-filmed clay particles enter the brine in the cavern they electrolytically flocculate and oil is sedimented to the cavern sump.

3.0 BACKGROUND DATA FOR ETZEL CAVERN K 117

Etzel is located in northern West Germany approximately 20 km southwest of Wilhelmshaven (fig. 1). Cavern K 117 is one of 33 caverns which have been leached in the salt dome at that site.

At present, this cavern has a total volume of slightly over 480,000 cubic meters and contains approximately 460,000 cubic meters of crude oil. A recent sonar caliper survey of the cavern is shown in fig. 2.

Filling of the cavern with petroleum began during the early stages of leaching, when 422 cubic meters of distillate heating oil were pumped in to serve as a protective blanket for the cemented 13 3/8-inch casing string. Filling of the cavern with crude oil began in September 1975 and continued until January 1977, at which time the cavern was, for all practical purposes, filled. With the exception of approximately 2,600 cubic meters of crude oil which were withdrawn during the earlier studies, there has been no transfer of oil into or out of the cavern since filling ceased (fig. 3).

Cavern K 117 contains a variety of crude oils, specifically:

- o Arabian Light;
- o Iranian Light;
- o Iranian Heavy;
- o Basrah; and
- o IVG Pool.

IVG Pool is an undifferentiable mixture of crude oils which had been stored temporarily at the NWKG tank farm near Wilhelmshaven. It consists of crude oil which had been pumped between different tanks and could contain any mixture of the following:

- o Arabian Light;
- o Arabian Heavy;
- o Iranian Light;
- o Iranian Heavy;
- o Nigerian Light;

- o Basrah; and/or
- o Khafji.

Typical analytical data for the crude oils stored at Etzel, including those in the IVG Pool mixture, are given in fig. 4. In fig. 5, the theoretical stratification of the various crude oils stored in cavern K 117 is shown. This is derived from data on the quantities of oil pumped into the cavern, incremental volumes of the cavern derived from sonar caliper surveys, and the oil/brine interface depth which was determined at regular intervals during cavern fill. Although fig. 5 depicts the cavern as containing discretely stratified crude oil, it is known from the earlier studies that mixing of the various layers has occurred to some extent.

4.0 SUMP SAMPLING OPERATIONS

Etzel cavern K 117 was completed with a 2 3/8-inch tubing string suspended within the 8 5/8-inch brine disposal string (fig. 6). The 2 3/8-inch tubing is used to inject river water into the 8 5/8-inch tubing following any removal of brine from the cavern to dilute the supersaturated brine and preclude salt bridging.

To minimize the workover operations necessary to obtain samples of the sump sediment, it was decided to construct a sampling device which could be lowered on a wireline through the 2 3/8-inch string. Zeinart Hydromechanic Co. constructed the device used in the sampling operations (figs. 7, 22, 23, and 24).

The sampling device constructed by Zeinart had the following characteristics:

- o A maximum outer diameter of 45 mm, which permitted free passage through the 2 3/8-inch (60 mm) tubing;
- o A beveled crown for cutting a core in the sediment;
- o Two different sample chambers — a small one for indurated or cemented sediments, and a relatively larger one for moderately soft sediments;
- o A core catcher consisting of spring metal leaves to prevent the sediment from falling out of the chamber during retrieval; and
- o A 50 kg drilling collar located above the sample chamber to impart an impact force large enough to obtain a core, even of indurated sediment.

The entire sampling operation was conducted on November 28, 1979. Prior to commencing the sampling operations, it was necessary to depressurize the 2 3/8-inch tubing, which took approximately two hours.

The sampling operation consisted of lowering the device through the 2 3/8-inch tubing until it touched the floor of the cavern. Having thus established the depth to the floor, the device was pulled up for between 20 and 30 meters and then allowed to free-fall to the cavern floor. The device was then pulled up to a height of 20 to 30 meters and again allowed to free-fall to the cavern floor. The device was pulled up and allowed to free-fall for a third time before being pulled back to the surface. On reaching the surface, the recovered sediment was placed in a brown glass bottle for storage and shipment to the laboratory.

The foregoing procedure was then repeated twice. The entire operation was completed in one day, and the samples were taken to the Preussag laboratory at Berkhöfen.

5.0 EXPERIMENTAL PROCEDURES

5.1 General Observations

A total of 140.30g of sediment were recovered. Of this total, 21.99g were sent to the U. S. Department of Energy's Bartlesville (Oklahoma) Energy Technology Center; 76.31g were used for determination of chemical composition and mineralogy; and the remaining 42.00g were used for determination of hydrocarbons.

The sediment sample comprised free salt crystals and other mineral grains in a small amount of a pale green, aqueous medium having a slightly milky, turbid appearance. The salt crystals were mostly colorless and transparent, although some of the other mineral grains were coated with an oily film. Rare crystals appeared to contain dark brown to black fluid-like inclusions. When shaken, some oil-like droplets would become apparent. The sample exuded a distinct petroleum odor.

5.2 Determination of Chemical Composition

A weighed portion of the sediment was dissolved in deionized water to produce a brine. The chemical composition of the sediment brine was then determined using the following analytical methods:

- o Sodium and potassium were determined by flame-emission photometry;
- o Chloride was determined by potentiometric titration; and
- o Magnesium, calcium, vanadium, nickel, copper, and iron were determined by atomic-absorption spectrometry.

5.2.1 Flame Emission Photometry. Sodium (Na) and potassium (K) were determined by standard flame-emission photometric methods. An air-propane flame was used and the radiation characteristic of Na and K isolated with appropriate interference filters. For Na, the emission at 589 nanometers was measured and for K, the emission at 767 nanometers was measured. Calibration curves were prepared using aqueous solutions of spectroscopic grade Na and K salts.

5.2.2 Atomic-Absorption Spectrometry. Atomic-absorption spectrometry was used to determine the concentration of calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), vanadium (V), and nickel (Ni) in the brine. For Ca and Mg,

atomization took place in an acetylene-compressed air flame. The trace metals, Cu, Fe, V, and Ni, were determined using a graphite furnace to achieve atomization. This permits a lower level of detection than is possible using the conventional flame atomization technique.

The salt content of the brine was too high for direct analysis of Ca and Mg by means of atomic-absorption, therefore these ions were determined after suitably diluting the solution with deionized water. The trace components were concentrated by chelation and liquid-liquid extraction prior to analysis.

Calibration curves were prepared using solutions of spectroscopic-grade salts obtained from the firms of E. Merck, Darmstadt, and Riedel-deHaen, Hannover. Chelation and liquid-liquid extraction of the trace metals were performed using appropriate salts and organic solvents (figs. 8 through 13).

All analyses were carried out using a Perkin-Elmer model 430 atomic-absorption spectrophotometer equipped with hollow-cathode lamps and, for the trace metals, a graphite furnace. Slit width, lamp current, air and acetylene settings, burner height, and wavelength were set according to manufacturers instructions and readjusted for each element.

5.2.3 Potentiometric Titration. To perform the potentiometric titration chloride determination, a 0.1N solution of silver nitrate was used. This was prepared by dissolving 16.9875g of silver nitrate in deionized water, acidifying with 2ml of 0.1N sulphuric acid, and diluting to 1.00 liter with deionized water.

The sediment brine was diluted so that its chloride concentration would be approximately 0.1N, acidified slightly, and then titrated potentiometrically using a silver wire as indicator and calomel half-element as a reference electrode. The titration was repeated three times.

5.3 Determination of Sediment Mineralogy

Bulk mineralogy of the sediment was determined using standard X-ray powder-diffraction techniques. A small amount of the homogenized sediment was pulverized in an agate mortar and applied as a thin smear to a glass plate using cellulose lacquer as an adhesive.

The sample mount was scanned from 16 to 68° two-theta, at 2° per minute, in a Philips diffractometer equipped with a proportional counter and lithium fluoride monochromator adjusted for $\text{CuK}\alpha^1(1.541\text{\AA})$. The X-ray tube was operated at 40kV and 40mA. The diffraction maxima were identified by reference to the standard powder diffraction data file (JCPDS, 1974).

5.4 Determination of Hydrocarbons

Initially, the sediment sample was heated to 120°C and the evolved gases collected in a cold trap. The equivalent of 5.9 ppm (weight) were recovered. Next the sediment was extracted quantitatively with tetrachloromethane, and the equivalent of 780 ppm (weight) recovered. The total hydrocarbon content of the sump sediment sample was equivalent to 786 ppm (weight).

The evolved gas was analyzed by gas chromatography, using a 1.8m stainless steel column packed with 15 percent OV-101 on Chromosorb-P, and flame ionization detection.

The tetrachloromethane extract was analyzed by both infrared spectroscopy and gas chromatography. The infrared analysis was performed with a double-beam spectrometer. The small volume of available sample precluded the use of a sealed demountable cell, so the analysis was made with the sample smeared on a potassium chloride window plate.

Gas chromatographic analysis of the extract was performed using a 50m OV-101 SCOT capillary column with both flame ionization and sulfur-specific flame photometric detection. The sample was further analyzed by a gas chromatographic simulated distillation method to determine the boiling range distribution of both the sulfur compounds and hydrocarbons.

6.0 RESULTS

Chemical analysis of the water-soluble portion of the sediment shows that it consists primarily of sodium and chloride, with minor to trace quantities of calcium, magnesium, and potassium; while the metals copper, iron, vanadium, and nickel are present in only minute amounts (fig. 14). On the basis of these results, the halite concentration in the sediment was determined to be approximately 95 percent. The moderately high concentration of calcium likely derives from solution of anhydrite, a minor constituent of the salt mass, and polyhalite and carnallite, which are present in trace quantities in the salt. Potassium and magnesium would also be attributable to the polyhalite and carnallite.

X-ray powder-diffraction analysis of the sediment also indicates that halite is the major constituent, with a subordinate amount of anhydrite and questionable traces of magnesite and gypsum (fig. 15). No polyhalite or carnallite were evident in the X-ray analysis of the sediment.

Gas chromatographic analysis of the sample evolved by heating the sediment to 120°C indicates that it consists of paraffinic hydrocarbons in the range propane (C₃) through octane (C₈) with the hexanes being dominant. Benzene and other aromatic hydrocarbons were not detected (figs. 16 and 17).

The infrared spectrum of the extract is typical of a weathered or topped crude (fig. 18). The series of bands between 810 and 672 cm⁻¹ together with other bands at 1605, 1460, 1380, 1160, 1075, 1035, 965, and 870 cm⁻¹ characterize the sample as a crude oil. Weathering of the sample is evidenced by the broad band between 3500 and 3100 cm⁻¹ which is typical of carboxylic acid; the strong carbonyl band at 1740 cm⁻¹; and the bands at 1270 and 1130 cm⁻¹ which are consistent with C=O stretch characteristic of carbonyls. There is no evidence in the spectrum for the presence of amines.

Capillary column gas chromatographic analysis of the tetrachloromethane extract clearly indicates that the sample is a topped or weathered crude oil (figs. 19 and 20). Flame ionization detection shows the presence of C₁₀ through C₄₀ with two maxima in the normal-paraffin distribution. The first maxima occurs at about C_{16/17} while the second occurs at about C₂₇. There is a slight minima at C₂₂. Pristane and phytane have a ratio of 1.07, which is typical of a crude oil of marine origin; while pristane/C₁₇ and phytane/C₁₈ exhibit ratios of 0.61 and 0.60, respectively, which are typical of an "intermediate base" crude oil. Flame photometric detection shows the presence of sulfur compounds throughout the C₁₄ to C₂₄ boiling range.

Gas chromatographic simulated distillation curves for both hydrocarbons and sulfur compounds are characteristic of a topped or weathered crude oil (fig. 21).

7.0 DISCUSSION

During development of the cavern it would be expected that the bulk of the sediment accumulating in the sump would consist of insoluble constituents of the salt, principally anhydrite and clay minerals. During quiescent storage additional sediment might accumulate as a result of fragments and slabs sloughing off the cavern walls.

Mineralogical and chemical analyses of the sump sediment sample support this latter contention. Halite comprises over 95 percent of the sediment, while anhydrite is a minor constituent, and other minerals are present in trace amounts only (figs. 14 and 15). This compares quite favorably with the bulk mineralogy of the salt mass determined by analysis of core material recovered during drilling of the cavern's developmental well:

Halite	- 95.58 percent
Anhydrite	- 3.56
Polyhalite	- 0.19
Clay minerals	- 0.67

Visual examination of the sump sediment sample revealed the presence of some well-formed halite crystals up to one-cm on an edge. Such large, well-formed crystals are typical of the salt mass.

The oil content of the sediment is believed to have resulted from adsorption of oil films onto clay particles which subsequently flocculated by electrolytic action of the brine. Clay particles, because of their surface activity, exhibit an affinity for oil. Sedimentation of oil from slicks by mineral matter has been recognized by several workers, notably McAuliffe and co-workers (1975), while laboratory studies by Poirier and Thiel (1941) also showed that oils may be sedimented by clay minerals. The flocculation behavior of hydrophobic sols in electrolytic solutions is well known (Van Olphen, 1963).

Clay particles are inherently present in crude oil, usually at concentrations of less than 0.1 percent. Clay is also a minor constituent of the Etzel salt dome, comprising an average of 0.67 percent. A further source of clay particles is the river water used to leach the cavern, periodically displace increments of the stored crude oil, and flush the oil-filled brine tubing string following cavern workover operations. This latter operation is likely to be responsible for most of the oil present in the sump sediments.

During well workover operations, if the 8 5/8-inch brine tubing string (fig. 6) is pulled and then reset it will fill

with oil. To displace this oil, several hundred cubic meters of river water are pumped down the string at a rate of approximately 300 cubic meters per hour. The mixing which occurs between the two phases during backwashing results in the clay particles becoming coated with a film of oil through adsorption. When the clay particles reach the brine, they electrolytically flocculate and oil is sedimented to the cavern floor.

Bassin and Ichiye (1977) calculated that, under ideal conditions of salinity and clay dispersion, from one-quarter to three grams of oil will be adsorbed by one gram of clay. On this basis, as little as 0.03 percent clay could account for the quantity of oil observed in the sediment sample. Bassin and Ichiye (1977) also confirmed Poirier's and Thiel's (1941) observations that globules of oil will wet to filmed clays, representing excess sedimentation capacity. Trace quantities of clay could, therefore, result in relatively significant quantities of oil being sedimented.

The rate of flocculation of hydrophobic sols is proportional to electrolyte concentration. Clay particles present in the river water used to leach the cavern or periodically displace increments of the stored crude oil would probably flocculate before they could adsorb an oil film.

Clay particles dispersed in the crude oil would likely adsorb an oil film while settling out but, in the absence of turbulence, interfacial tension at the oil/brine boundary would prevent these particles entering the brine phase and flocculating. The boundary layer observed in this cavern, and reported in the earlier studies (KBB, Inc., 1979) is enriched in sediment which is believed to have settled out of the crude oil.

The composition of the oil as determined by infrared spectroscopy, gas chromatography, and simulated distillation, does not support the settling of heavy asphaltic compounds. Microscopic observations of the sediment after it was solvent-extracted revealed negligible inclusions, of what might be oil, in salt crystals.

Oxygen dissolved in the river water used in flushing the brine tubing string would contribute to the weathering of the oil evidenced by the presence of carbonyl and carboxylic acid bands in the infrared spectrum of the sediment extract. Auto-oxidation of oil is generally a slow process, but dispersion could result in a relative increase in the rate of reaction. Iron catalyzes auto-oxidation of hydrocarbons (Thompson, oral commun., 1976), hence rust inside the brine tubing could also contribute to an increase in the reaction rate.

8.0 CONCLUSION

Turbid river water used to flush oil out of the brine tubing string following workover operations has resulted in petroleum becoming sedimented to the floor of Etzel cavern K 117. The oil is believed to be filmed on clay particles which have electrolytically flocculated. The amount of oil sedimented is insignificant relative to the volume stored in the cavern; however, it represents a significant fraction of the uppermost layer of sump sediments.

Other studies (Bassin and Ichiye, 1977) indicate that oil-filmed clay floccules are stable in dynamic environments. It seems unlikely that significant petroleum would be displaced to the surface during cavern operations as a result of desorption from the clay, or deflocculation and resuspension of the oil-filmed clay particles.

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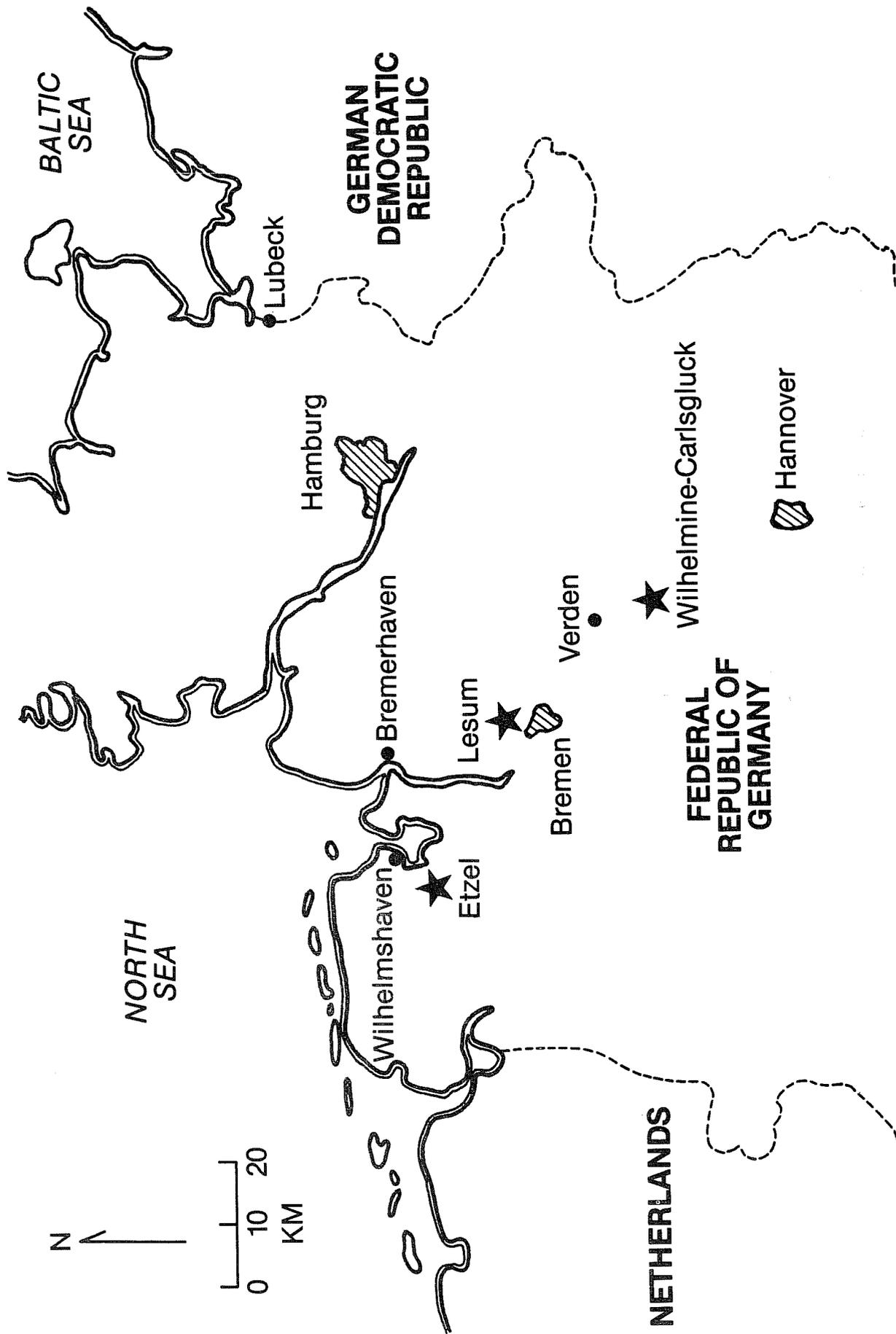


Figure 1. Outline map of northern West Germany.

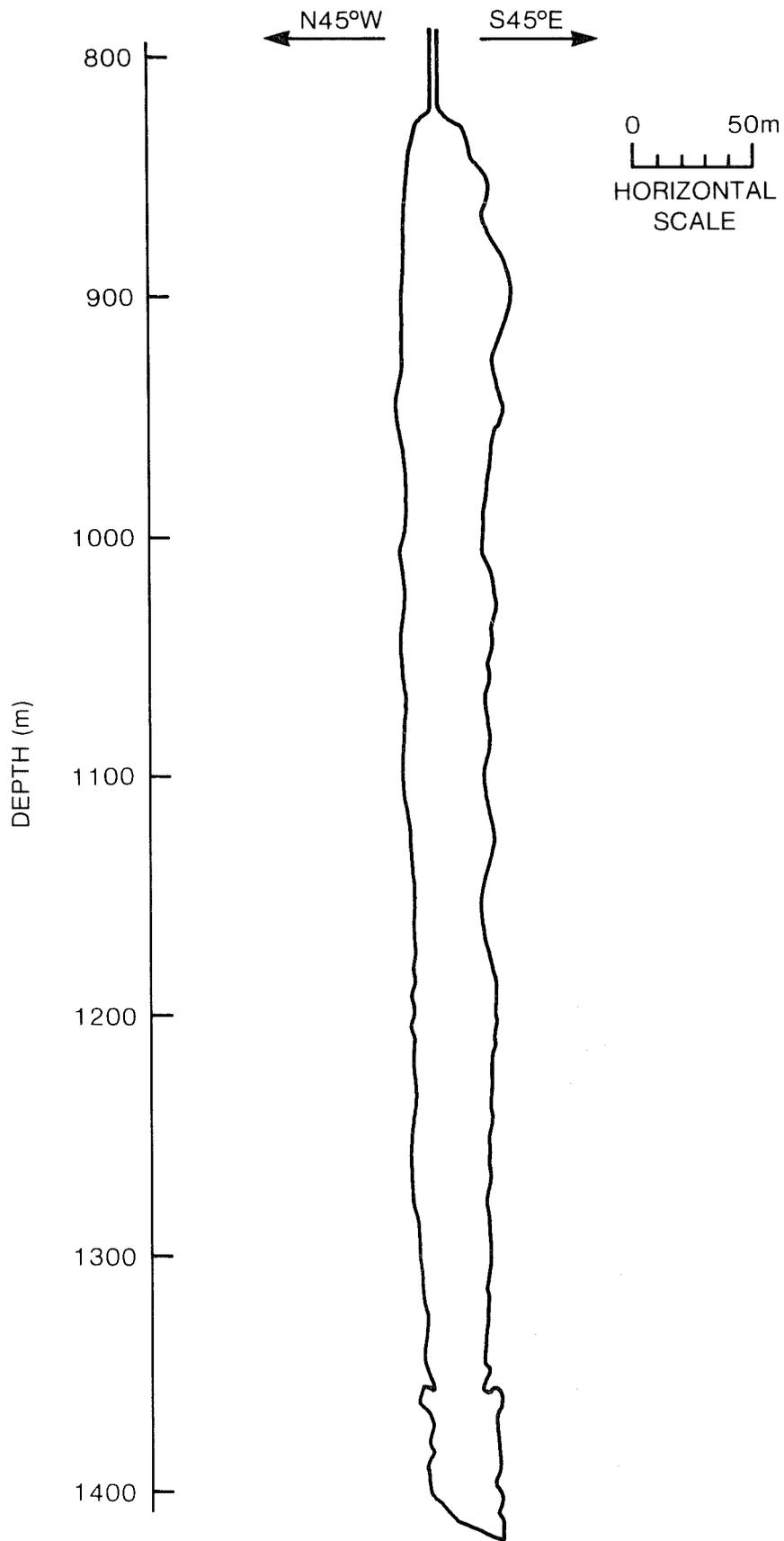


Figure 2. Sonar caliper survey of Etzel cavern K 117.

Date Stored (month/year)	Quantity Stored (m ³)	Cumulative Quantity (m ³)	Type Oil
7/74 - 8/75	422	422	Distillate heating oil
9/75 - 12/75	18,829	19,251	Arabian Light crude oil
1/76	14,224	33,475	Iranian Light crude oil
1/76	61,083	94,558	Basrah crude oil
1/76 - 4/76	11,391	105,949	Crude oil composite
4/76 - 5/76	44,454	150,403	Arabian Light crude oil
6/76 - 7/76	38,328	188,731	Iranian Heavy crude oil
7/76 - 8/76	25,338	214,069	Arabian Light crude oil
9/76	93,662	307,731	Iranian Heavy crude oil
10/76 - 11/76	12,389	320,120	Crude oil composite
12/76	40,826	360,946	Iranian Heavy crude oil
12/76	54,871	415,817	Crude oil composite
1/77	44,830	460,647	Arabian Light crude oil

Figure 3. Crude oil inventory of Etzel cavern K 117.

Crude oil	Density (g/cm ³) at 15°C	Kinematic Viscosity (centi-Stokes) at 10°C	at 30°C	Water content (Wt. %)	Salt content (ppm)	Vapor pressure (bar)	Sulfur content (Wt. %)
Arabian Light	0.857	13.2	7.2	0.1	26.7	0.30	1.69
Arabian Medium	0.871	28.3	12.8	0.1	29.5	0.38	2.27
Arabian Heavy	0.888	59.6	26.3	0.1	19.0	0.44	2.67
Khafji	0.885	50.1	21.5	0.1	52.6	0.57	2.69
Basrah	0.854	14.1	7.6	0.1	16.2	0.41	1.92
Iranian Light	0.857	15.2	7.6	0.1	32.4	0.39	1.38
Iranian Heavy	0.870	22.9	11.1	0.1	40.0	0.36	1.73

All data derived from tanker offloading reports.

Figure 4. Inspection data for crude oils stored at Etzel.

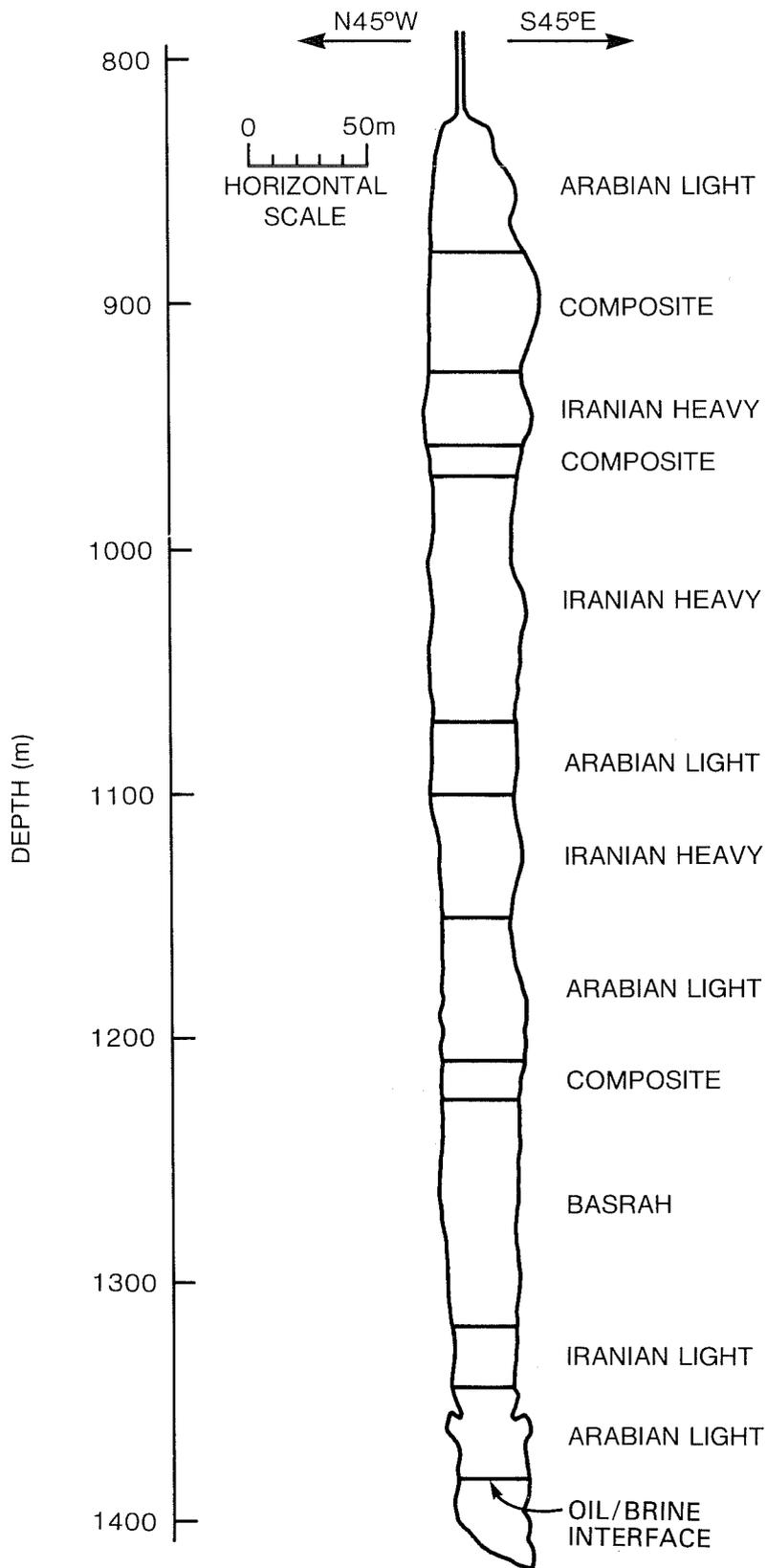


Figure 5. Theoretical stratification of crude oil in Etzel cavern K 117.

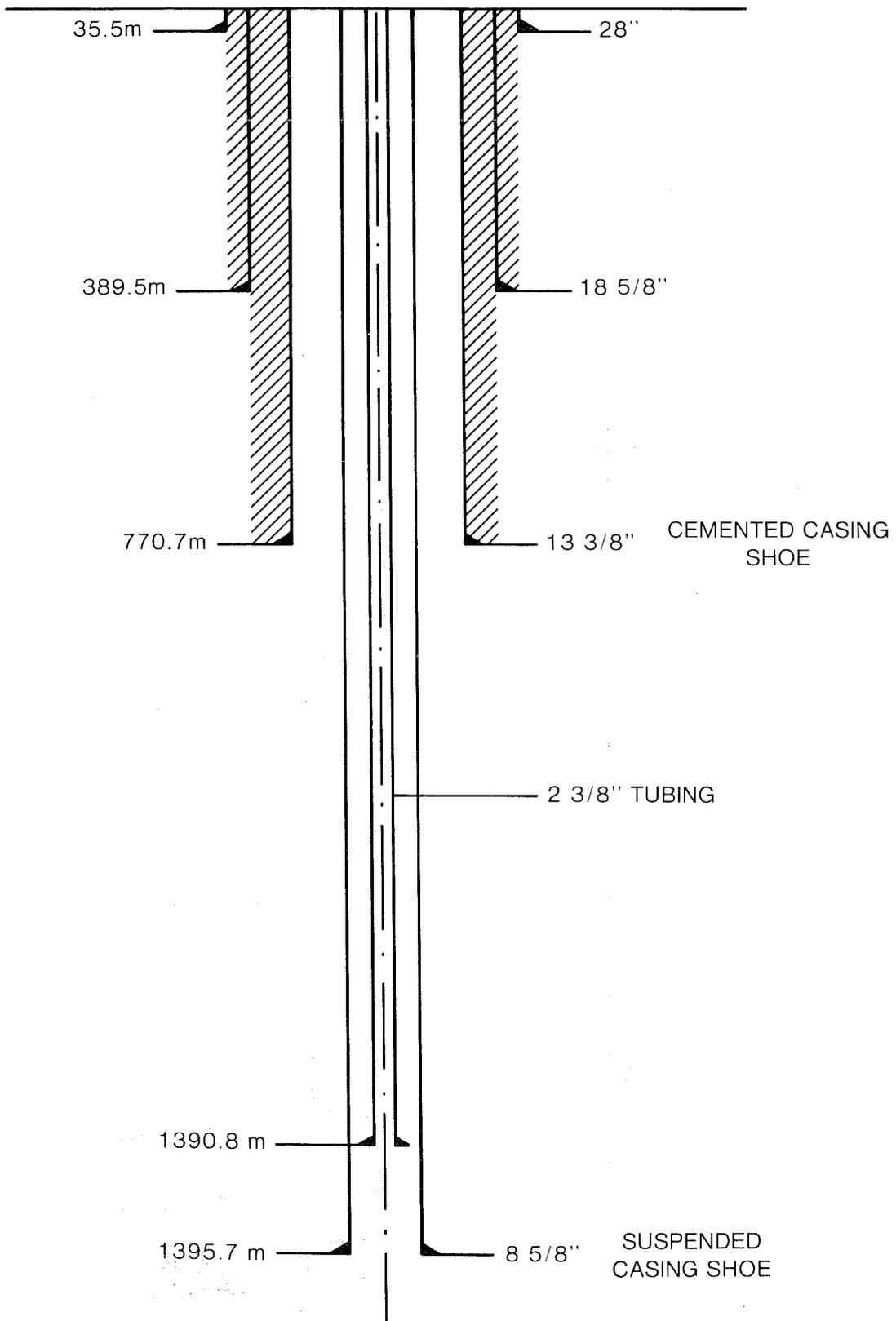


Figure 6. As-built drawing for Etzel cavern K 117.

DIMENSIONS ARE IN MILLIMETERS

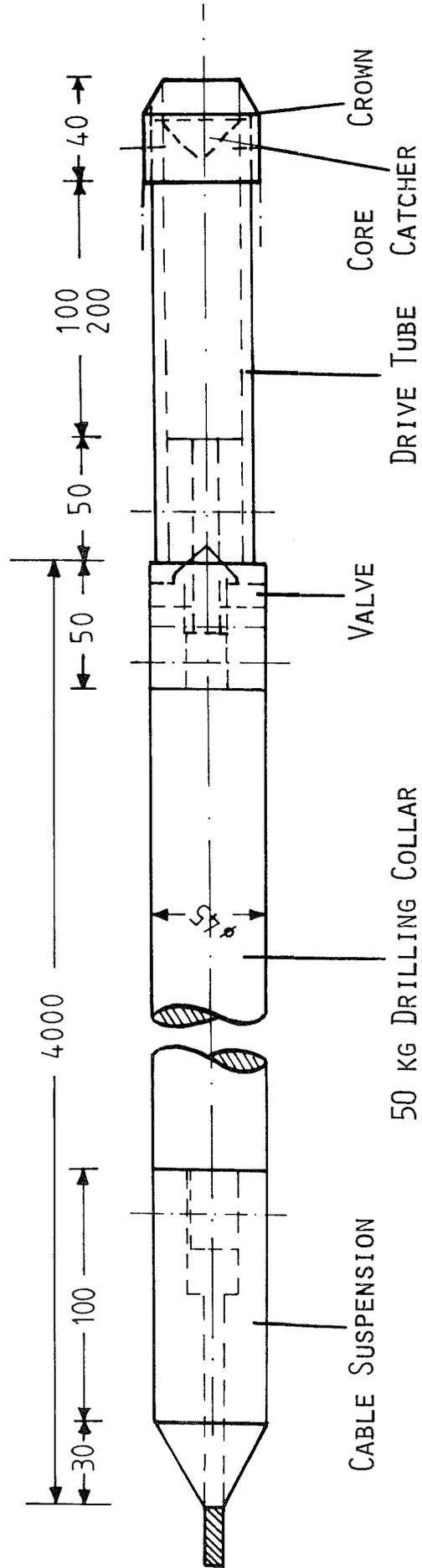
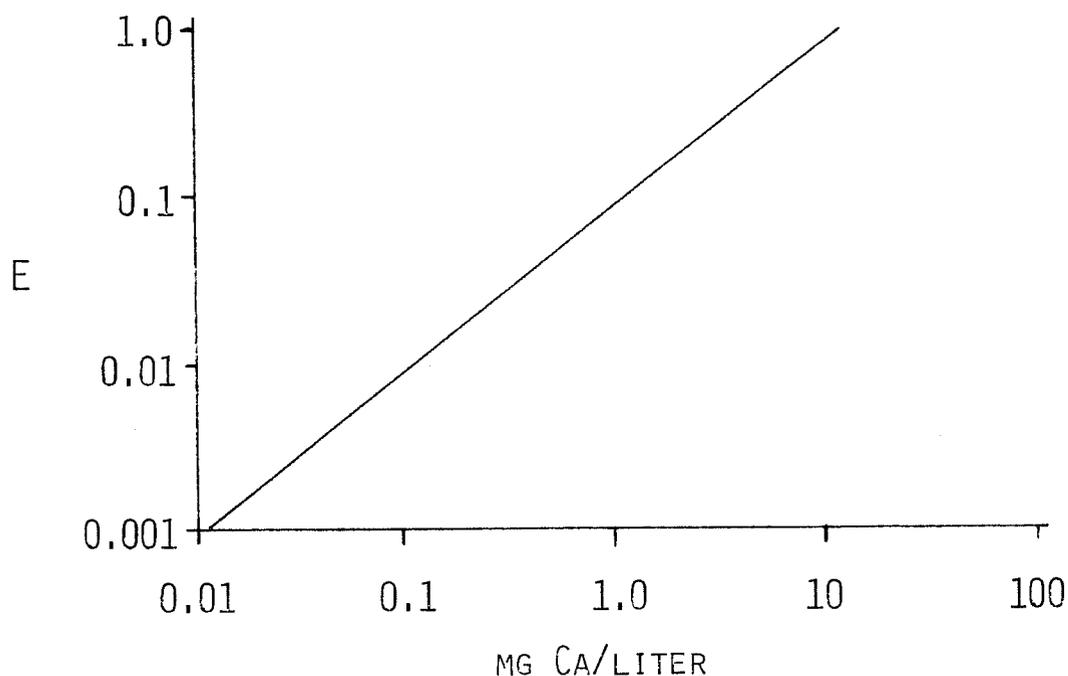


Figure 7. Device used for sampling sump sediments in Etzel cavern K 117.

Stock Solution:

2.497 g of spectroscopic grade CaCO_3 were dissolved in 5 ml of concentrated HCl. This solution was diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter Ca. Dilutions of the stock Ca solution to be used as calibration standards were made at the time of analysis. Because of the relatively low concentration of interfering elements, lanthanum was not added.

Calibration Curve:



Wavelength: 422.7 nm

Sensitivity: 0.045 mg Ca/liter for $E = 0.004$

Detection limit: 0.002 mg Ca/liter

Accuracy: ± 1.0 mg in the range 10 - 100 mg/liter

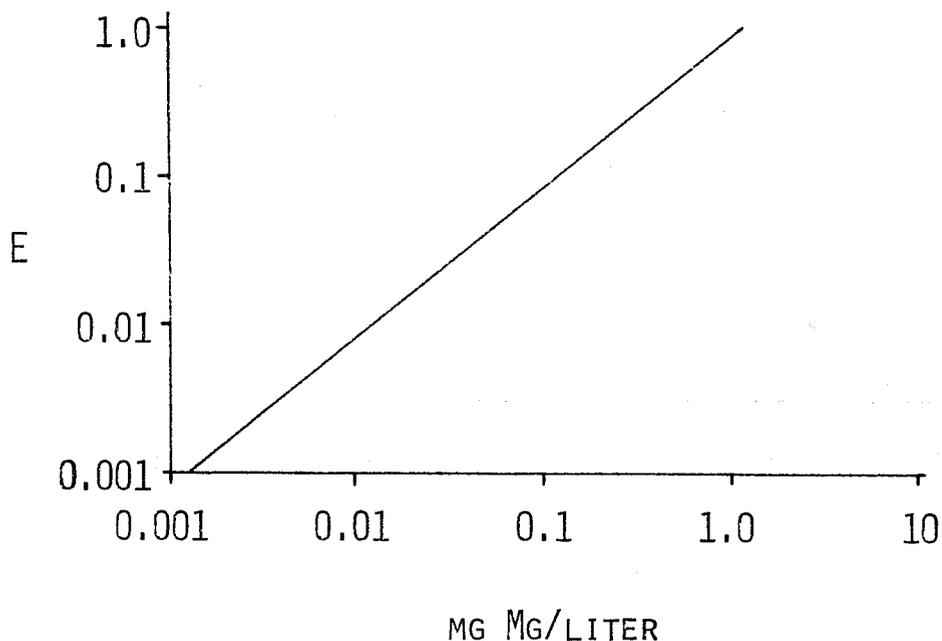
± 0.1 mg in the range 1 - 10 mg/liter

Figure 8. Atomic-absorption spectroscopic determination of calcium.

Stock Solution:

1.658 g of spectroscopic grade MgO were dissolved in 10 ml of redistilled HNO₃ and diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter Mg. Dilutions of the stock Mg solution to be used as calibration standards were made at the time of analysis. Because of the relatively low concentration of interfering elements, lanthanum was not added.

Calibration Curve:



Wavelength: 285.2 nm
Sensitivity: 0.0045 mg Mg/liter for E = 0.004
Detection limit: 0.0004 mg Mg/liter
Accuracy: ±0.05 mg in the range 0.001 - 10 mg/liter

Figure 9. Atomic-absorption spectroscopic determination of magnesium.

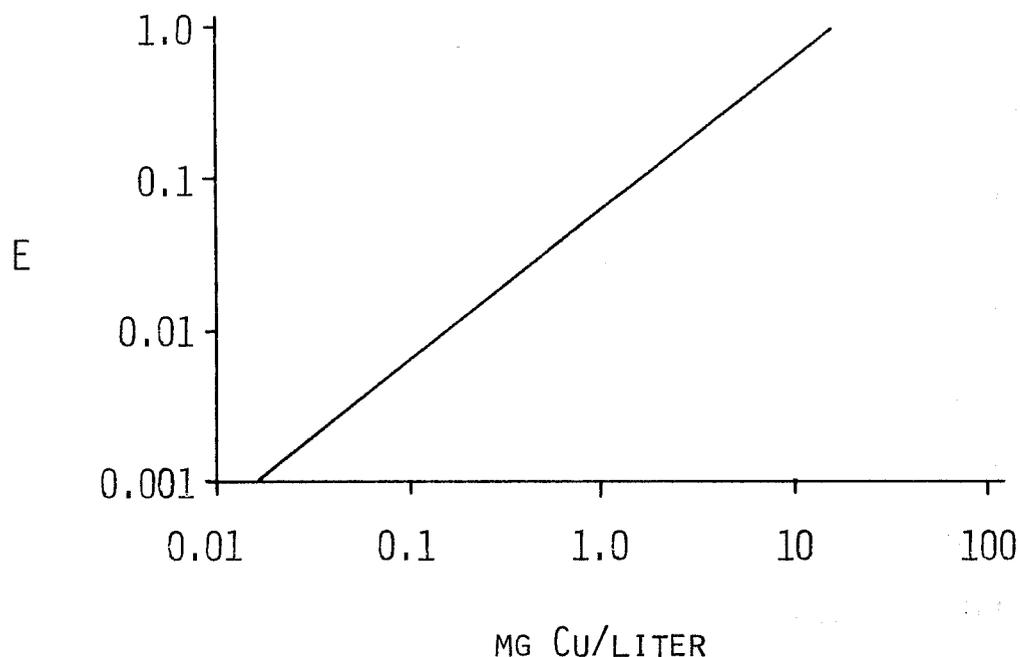
Stock Solution:

1.000 g of spectroscopic grade electrolyte copper was dissolved in 4 ml of redistilled HNO_3 and diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter Cu. Dilutions of the stock Cu solution to be used as calibration standards were made at the time of analysis.

Extraction:

Copper was chelated with ammonium pyrrolidine dithiocarbamate and extracted with methyl isobutyl ketone. The organic extract was analyzed by means of a graphite furnace.

Calibration Curve:



Wavelength: 324.7 nm
Sensitivity: 0.053 mg Cu/liter for $E = 0.004$
Detection limit: 0.003 mg Cu/liter
Accuracy: ± 0.1 mg in the range 0.01 - 10 mg/liter
 ± 1.0 mg in the range 10 - 100 mg/liter

Figure 10. Atomic-absorption spectroscopic determination of copper.

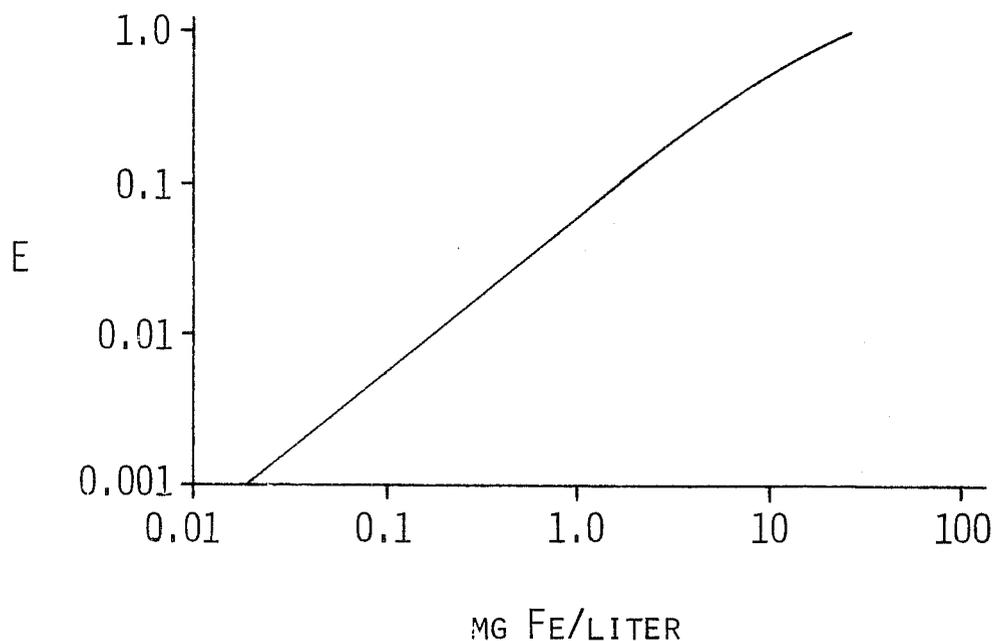
Stock Solution:

1.000 g of spectroscopic grade iron wire was dissolved in 5 ml of redistilled HNO_3 and diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter of Fe. Dilutions of the stock Fe solution to be used as calibration standards were made at the time of analysis.

Extraction:

Iron was chelated with sodium diethyldithiocarbamate and extracted with methyl isobutyl ketone. The organic extract was analyzed by means of a graphite furnace.

Calibration Curve:



Wavelength: 248.3 nm

Sensitivity: 0.071 mg Fe/liter for $E = 0.004$

Detection limit: 0.003 mg Fe/liter

Accuracy: ± 0.05 mg in the range 0.01 - 10 mg/liter

± 1.0 mg in the range 10 - 100 mg/liter

Figure 11. Atomic-absorption spectroscopic determination of iron.

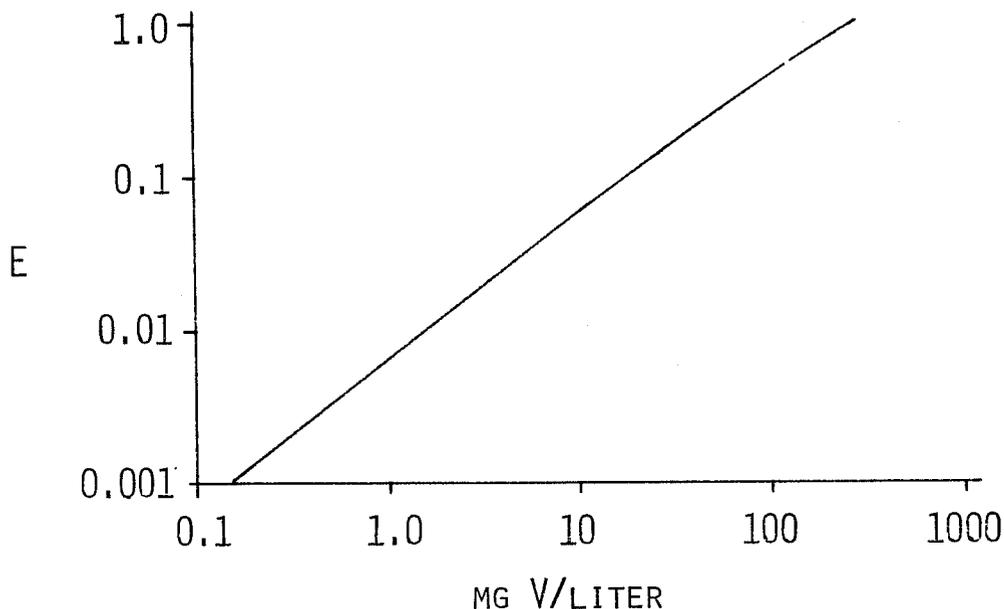
Stock Solution:

2.296 g of spectroscopic grade NH_4VO_3 were dissolved in 20 ml of dilute HCl and further diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter V. Dilutions of the stock V solution to be used as calibration standards were made at the time of analysis.

Extraction:

Vanadium was chelated with cupferron and extracted with chloroform. The organic extract was analyzed by means of a graphite furnace.

Calibration Curve:



Wavelength: 318.4 nm
Sensitivity: 0.75 mg V/liter for $E = 0.004$
Detection limit: 0.05 mg V/liter
Accuracy: ± 0.5 mg in the range 1 - 30 mg/liter
 ± 1.0 mg in the range 30 - 130 mg/liter

Figure 12. Atomic-absorption spectroscopic determination of vanadium.

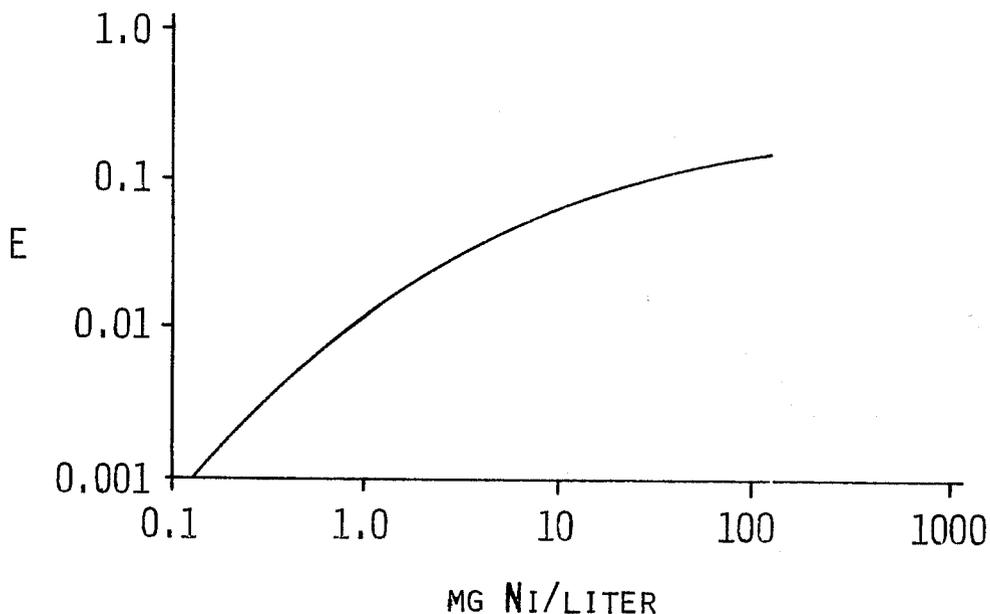
Stock Solution:

4.953 g of spectroscopic grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water, acidified with 10 ml of concentrated HNO_3 and diluted to 1,000 ml with deionized water, yielding a solution containing 1,000 mg/liter Ni. Dilutions of the stock Ni solution to be used as calibration standards were made at the time of analysis.

Extraction:

Nickel was chelated with ammonium pyrrolidine dithiocarbamate and extracted with methyl isobutyl ketone. The organic extract was analyzed by means of a graphite furnace.

Calibration Curve:



Wavelength: 352.4 nm
Sensitivity: 0.34 mg Ni/liter for $E = 0.004$
Detection limit: 0.02 mg Ni/liter
Accuracy: ± 3 mg in the range 10 - 100 mg/liter

Figure 13. Atomic-absorption spectroscopic determination of nickel.

COMPONENT	CONCENTRATION
Sodium	391.3 g/kg
Potassium	100 ppm
Magnesium	300 ppm
Calcium	1,300 ppm
Chloride	606 g/kg
Vanadium	<0.05 ppm
Nickel	<0.02 ppm
Copper	0.05 ppm
Iron	0.02 ppm
Insoluble matter	4.43 Wt. %

Figure 14. Composition of the water-soluble sediment.

dÅ (obs.)	Relative Intensity	Peak Assignment
4.29	1	Gypsum
3.88	12	Anhydrite
3.51	100	Anhydrite
3.27	8	Halite
3.42	3	Anhydrite
3.02	1	Gypsum
2.85	40	Anhydrite
2.82	78	Halite
2.75	2	Magnesite(?)
2.471	13	Anhydrite
2.330	21	Anhydrite
2.204	20	Anhydrite
2.186	19	Anhydrite
2.086	8	Anhydrite
1.993	52	Anhydrite/Halite
1.940	4	Anhydrite
1.868	22	Anhydrite
1.856	5	Anhydrite
1.748	39	Anhydrite
1.746	24	Anhydrite
1.700	2	Halite
1.647	12	Anhydrite
1.630	12	Halite
1.596	2	(?)
1.567	6	Anhydrite
1.526	6	Anhydrite
1.490	11	Anhydrite
1.426	3	Anhydrite
1.410	7	Halite
1.397	4	Anhydrite

Figure 15. X-ray mineralogy of the sediment.

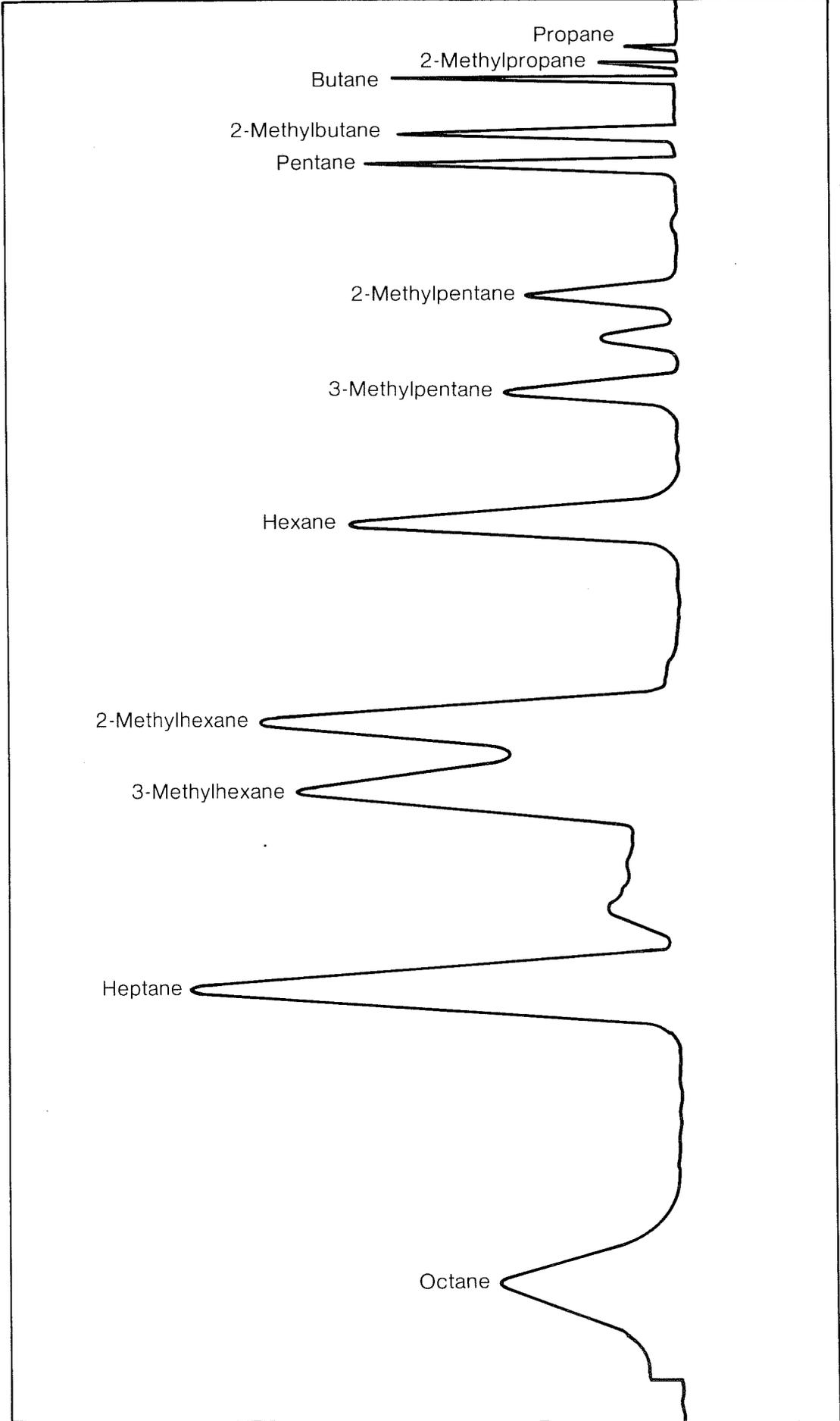


Figure 16. Gas chromatogram of the evolved hydrocarbons.

COMPONENT	CONCENTRATION (ppm)
Propane	0.01
2-Methylpropane (<i>iso</i> -Butane)	0.02
Butane	0.06
2-Methylbutane (<i>iso</i> -Pentane)	0.15
Pentane	0.17
2-Methylpentane (<i>iso</i> -Hexane)	0.17
3-Methylpentane (<i>anteiso</i> -Hexane)	0.21
Hexane	0.55
2-Methylhexane (<i>iso</i> -Heptane)	1.18
3-Methylhexane (<i>anteiso</i> -Heptane)	1.04
Heptane	1.44
Octane	0.90

Figure 17. Composition of the evolved hydrocarbons.

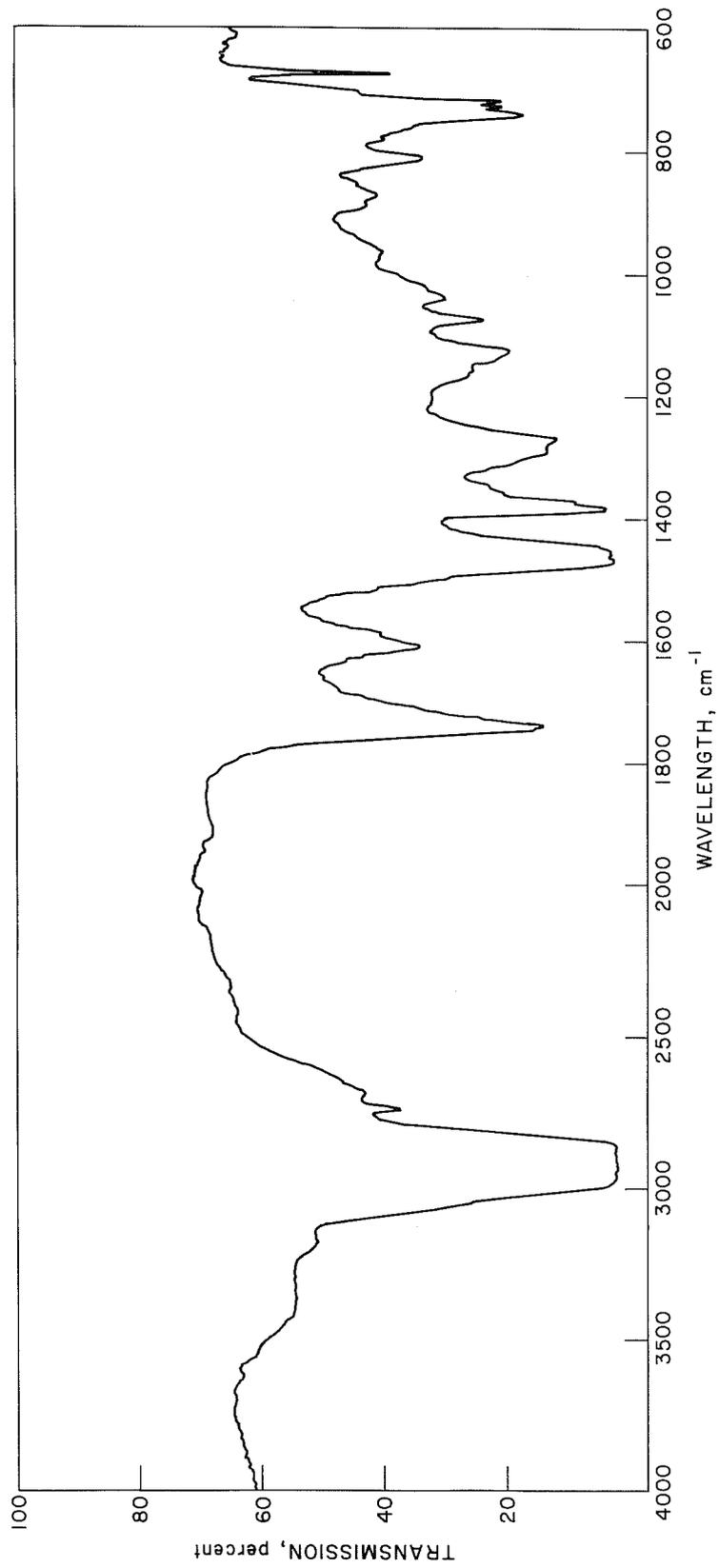


Figure 18. Infrared spectrum of the tetrachloromethane extract.

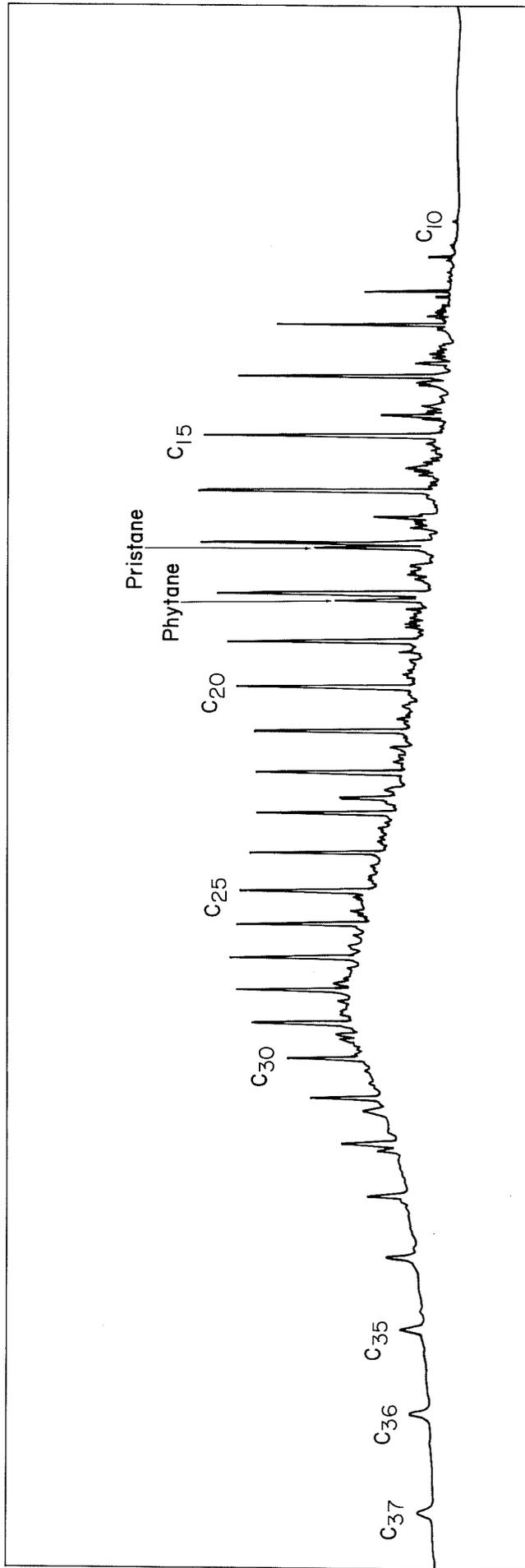


Figure 19. Gas chromatogram of the tetrachloromethane extract using flame ionization detection.

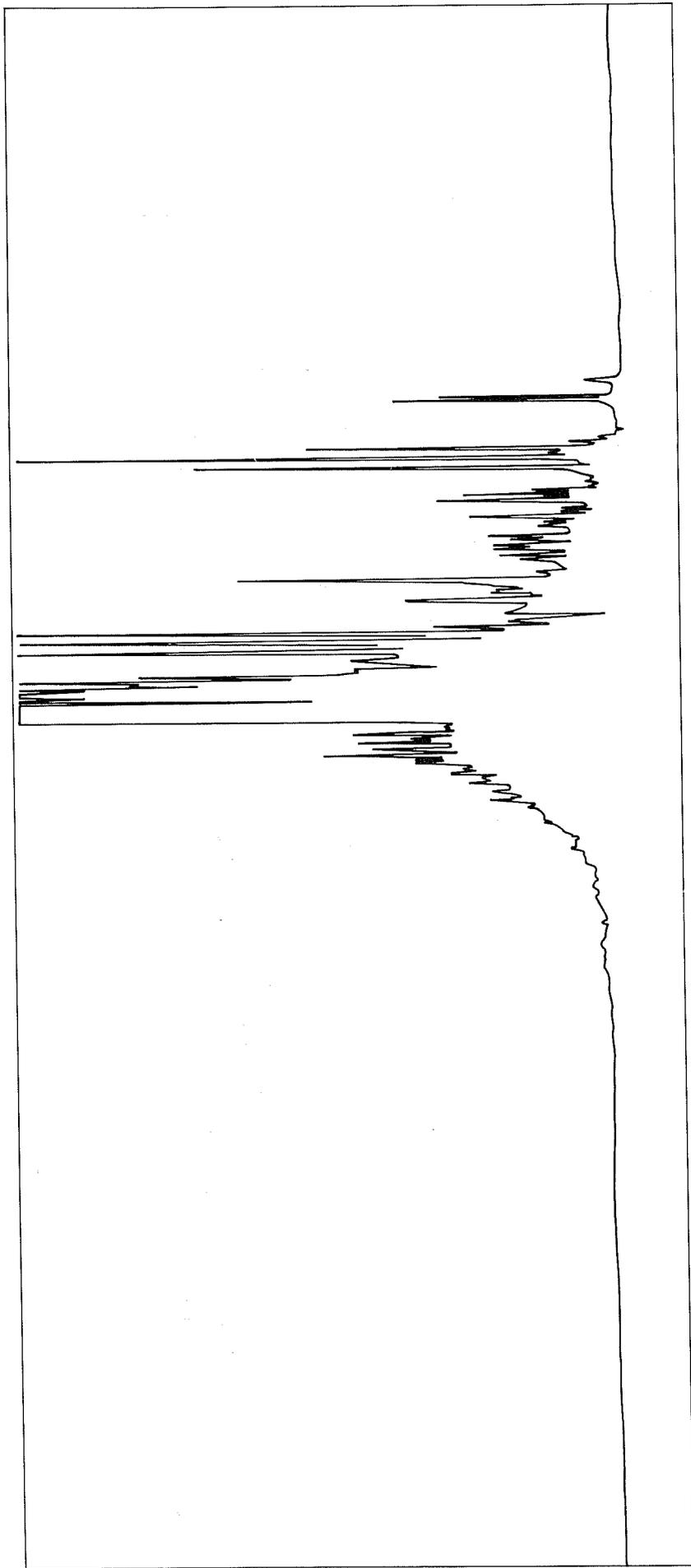


Figure 20. Gas chromatogram of the tetrachloromethane extract using sulfur-specific flame photometric detection.

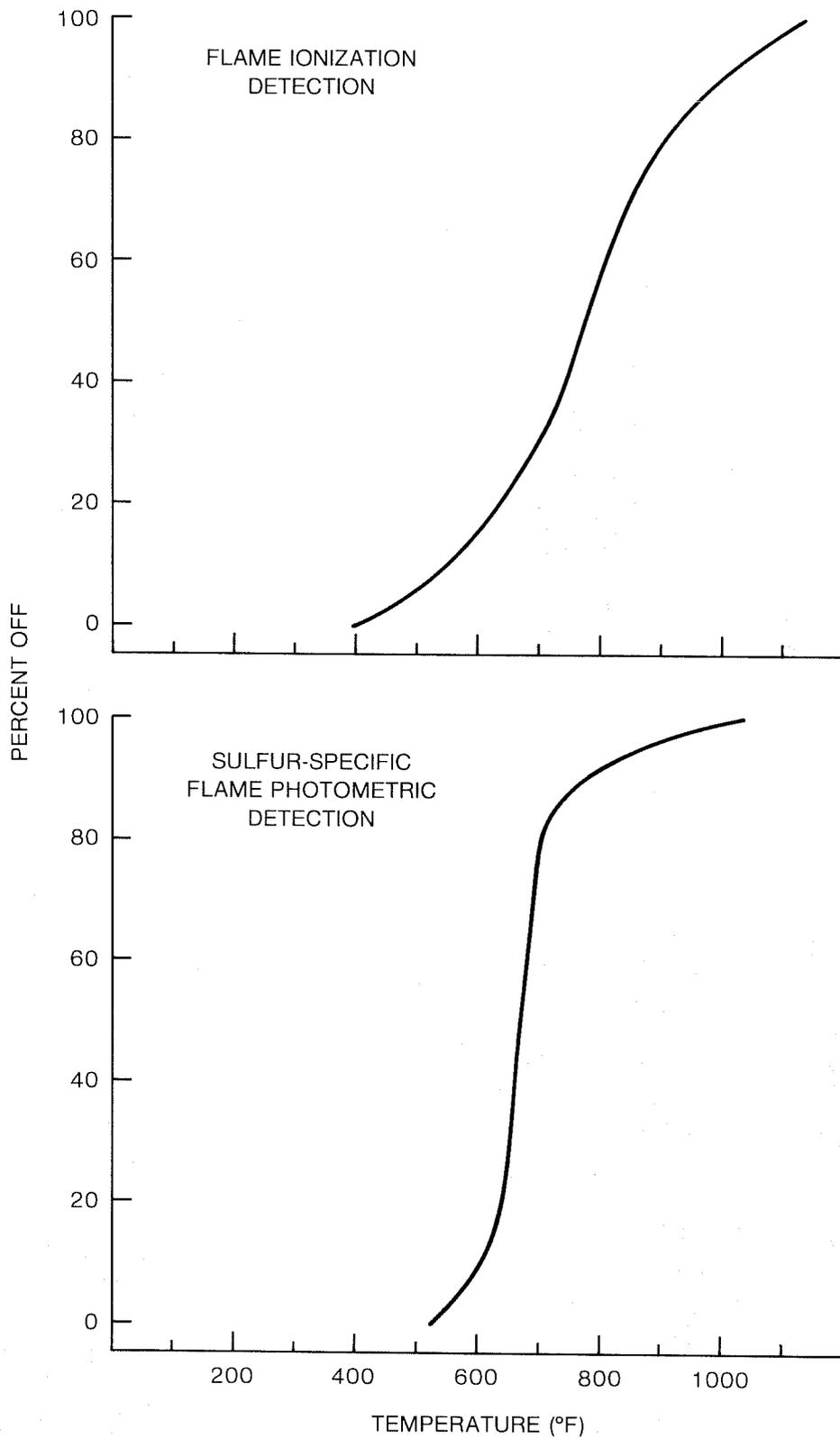


Figure 21. Gas chromatographic simulated distillation of the tetrachloromethane extract.





Figure 23. Sampling device about to be lowered into Etzel cavern K 117.



Figure 24. Core catcher and crown of sampling device.

