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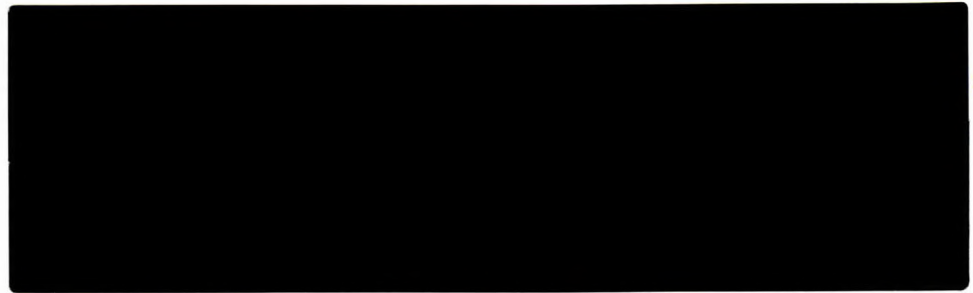
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Canada Centre for
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INVESTIGATIONS OF THE APPLICABILITY OF
MAGNETIC RESONANCE IMAGING METHODS
TO CANMET'S RESEARCH INTERESTS
PART THREE: RESULTS FROM UBC BRUKER MSL 400

C. A. MacConnachie and L. H. Randall
Division Report WRC 92-59 (TR)

August 1992

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INVESTIGATIONS OF THE APPLICABILITY OF MAGNETIC RESONANCE IMAGING METHODS TO CANMET'S RESEARCH INTERESTS PART THREE: RESULTS FROM UBC BRUKER MSL 400

C.A. MacConnachie* and L.H. Randall**

ABSTRACT

This report is part three of a three-part report on the status of magnetic resonance imaging activity at WRC. This report discusses in detail the results of the experiments carried out at the University of British Columbia (UBC) chemistry department June 30th to July 6th 1992. All NMR measurements reported here were carried out on a 9.4T/400 MHz. Bruker MSL 400 spectrometer equipped with a microimaging system. Selected images and their corresponding spectra are presented and discussed. Conclusions on the types of experiments feasible with such an instrument are outlined.

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TROISIÈME PARTIE DES ÉTUDES SUR L'APPLICABILITÉ DES
MÉTHODES D'IMAGERIE PAR RÉSONANCE MAGNÉTIQUE
AUX ACTIVITÉS DE RECHERCHE DE CANMET :
RÉSULTATS DES EXPÉRIENCES EFFECTUÉES SUR LE BRUKER MSL 400 DE L'UBC

C.A. MacConnachie et L.H. Randall[*]

RÉSUMÉ

Le présent rapport est le troisième d'une série de trois rapports portant sur l'état des travaux effectués dans le domaine de l'imagerie par résonance magnétique au CRO. Il contient une présentation détaillée des résultats des expériences effectuées au département de chimie de l'University of British Columbia (UBC) du 30 juin au 6 juillet 1992. Toutes les mesures de RMN dont il est question dans ce rapport ont été effectuées sur un spectromètre Bruker MSL 400, 9,4 T/400 MHz, muni d'un système de micro-imagerie. Des images sélectionnées et leurs spectres sont présentés et analysés. Des conclusions concernant les types d'expériences réalisables avec cet instrument sont décrites.

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FIGURES

FIGURES (cont)

EXPERIMENTAL

All NMR measurements were made on a high field solution/solid-state Bruker MSL 400 spectrometer located at the University of British Columbia. The instrument was equipped with a micro imaging system. The probe used in these studies was the proton imaging probe supplied by Bruker with a 12-mm coil. The spin echo pulse sequence was used to determine the average spin-spin relaxation times. The inversion recovery pulse sequence was used to determine the average T_1 spin lattice relaxation times for the samples.

After determining the approximate relaxation times, it was determined that both spin echo imaging and chemical shift selective image sequences would be feasible for the samples studied. Spin echo imaging employs no chemical shift selection, but provides T_2 discrimination in the image. Chemical shift selective imaging employs a different pulse sequence - the "C4S" sequence. Grey scale images were impossible to produce due to the untimely breakdown of the graphic display processor unit.

DISCUSSIONS OF RESULTS

Sample 1 was a very viscous UTF water-in-oil emulsion. High viscosity means that the oil component of the fluid has a very short T_2, on the order of a millisecond and will not be observed in a spin echo experiment in which the echo time is longer than approximately 5 ms. A 1-D NMR spectrum of the sample is shown in Fig. 1. The oil peak is the broad up-field resonance and the water peak is the much narrower down-field signal. The long T_2 of

the water component relative to the oil component is reflected in the dramatic difference in the line widths of the two peaks.

A spin echo imaging experiment performed on this sample is shown in Fig. 2. The echo time used was 7.8 ms. The in-plane resolution achieved was 51 μm while the slice thickness was 600 μm. The gradient strengths employed were 6 - 10 G/cm, the recovery time was 3 s, and four scans were collected on each increment. The total time for collection of this experiment was 51 minutes. The water distribution is relatively uniform throughout the sample. There are, however, regions in the sample in which the water concentration is much higher than the average. Small droplets of water resulting from the aggregation of the emulsified water explain the results in the image. Individual emulsified droplets of water are not visible in the image of the sample. This means that either the emulsified water droplets are smaller 50 μm or that the diffusion of water is sufficiently high to reduce the real resolution to far less than what is experimentally achievable.

Figure 3 shows a spin echo image obtained from a froth flotation sample. This image is drastically different from that in Fig. 2. The echo time used was 6.8 ms, the in-plane resolution was 51 μm, and the slice thickness was 600 μm. The recovery time used was 1 s and 16 scans were collected. The total time for collection of the image was 68 minutes. The water phase appears distinct and separate from the oil phase and is thus not in an emulsified state. There are small areas where the concentration of water is higher in the water region and this can be attributed to small aggregated droplets of water. This sample is clearly more heterogeneous than the first and it is possible to selectively image the oil or the water phase .

No dynamic processes were present in the previous two samples. The third sample examined was a gasoline emulsion sample containing gasoline, ethanol, water, and a surfactant whose composition is unknown. The sample separates into distinct layers over time on the order of hours. Several peaks are observed in the NMR spectrum and are not characterized as yet. It was determined in this study that the species present have very different T_1 and T_2 relaxation times and these differences indicate different physical and/or chemical environments. An in-depth study of model emulsion systems in which the chemical constituents are known and well characterized could provide uniquely interesting information about separation processes in emulsions. Figure 4 shows a 1-D NMR spectrum of the emulsion using an inversion recovery sequence. One species has a very short relaxation time compared with the other species. Using a chemically selective pulse sequence, we were able to select only this component and minimize the contributions to the signal form the other species present. The 1-D NMR spectrum collected with this chemically selective pulse sequence can be seen in Fig. 5 and compared to Fig. 4.

The chemical shift images collected on this gasoline emulsion are shown in Fig. 6, 7, and 8. The echo time used was 15.8 ms, the in-plane resolution was 51 μm, and the slice thickness was 600 μm. The gradients were on the order of 6 - 10 G/cm. The recovery time was 600 ms and the number of scans was 16 resulting in a total time for collection of each image of 14 minutes. The sample was shaken vigorously to cause the sample to form an opaque, gel-like emulsion. A series of chemically selective images were collected over a 12-hour period. Images taken during this time period show that the compound was fairly well distributed over the entire sample volume. There are, however, large regions where no signal

arises from the sample. This was likely due to air bubbles entrained in the emulsion as it was shaken. After 12 hours of imaging, chemical shift artifacts had appeared in the images and this is due to the changes in relaxation behaviour of the components of the sample. The relaxation behaviour of the components in the sample change over time and this indicates that the chemical and/or physical nature of the compounds changes as the mixture of components demulsifies.

Whole oil sands sludge samples were investigated by high-resolution proton NMR spectroscopy at 400 MHz but were found to have relaxation times too short to be investigated by NMR microscopy. The signals were found to be on the order of 1000 Hz wide, making spatial isolation of the signal into voxels or pixels smaller than the sample size impossible with the techniques currently available on this spectrometer.

The final sample examined was a water-in-oil emulsion from the OSLO process. The sample contained additives and the droplet size of the emulsified water was found to be <-30 μm by optical microscopy. The 1-D proton NMR spectrum in Fig. 9 shows that the major species in solution have reasonably long T_2 relaxation times. Figure 10 shows a chemical shift selective image obtained on the sample. The echo time used was 15.8 ms, the in plane resolution was 51 μm, and the slice thickness was 600 μm. The recovery time used was 5 s and the number of scans taken on each phase increment was 24 resulting in a total collection time of 512 minutes. The water distribution was almost completely uniform across the sample as expected but there were small regions in which the concentration of water was lower than in others.

CONCLUSIONS

Chemical shift selective imaging of fluid samples under conditions of high resolution is possible. The real resolution obtained in the NMR imaging experiment is governed in part by the diffusion coefficient of the species under study and is of course affected by its physical and chemical conditions. Using NMR imaging, the spatial distribution and chemistry of various chemical components can be monitored as a function of time. Studies that hold the most promise are those in which a dynamic process is occurring in which the chemical and physical interactions of the various components can be monitored by both 1-D NMR spectroscopy and NMR imaging.
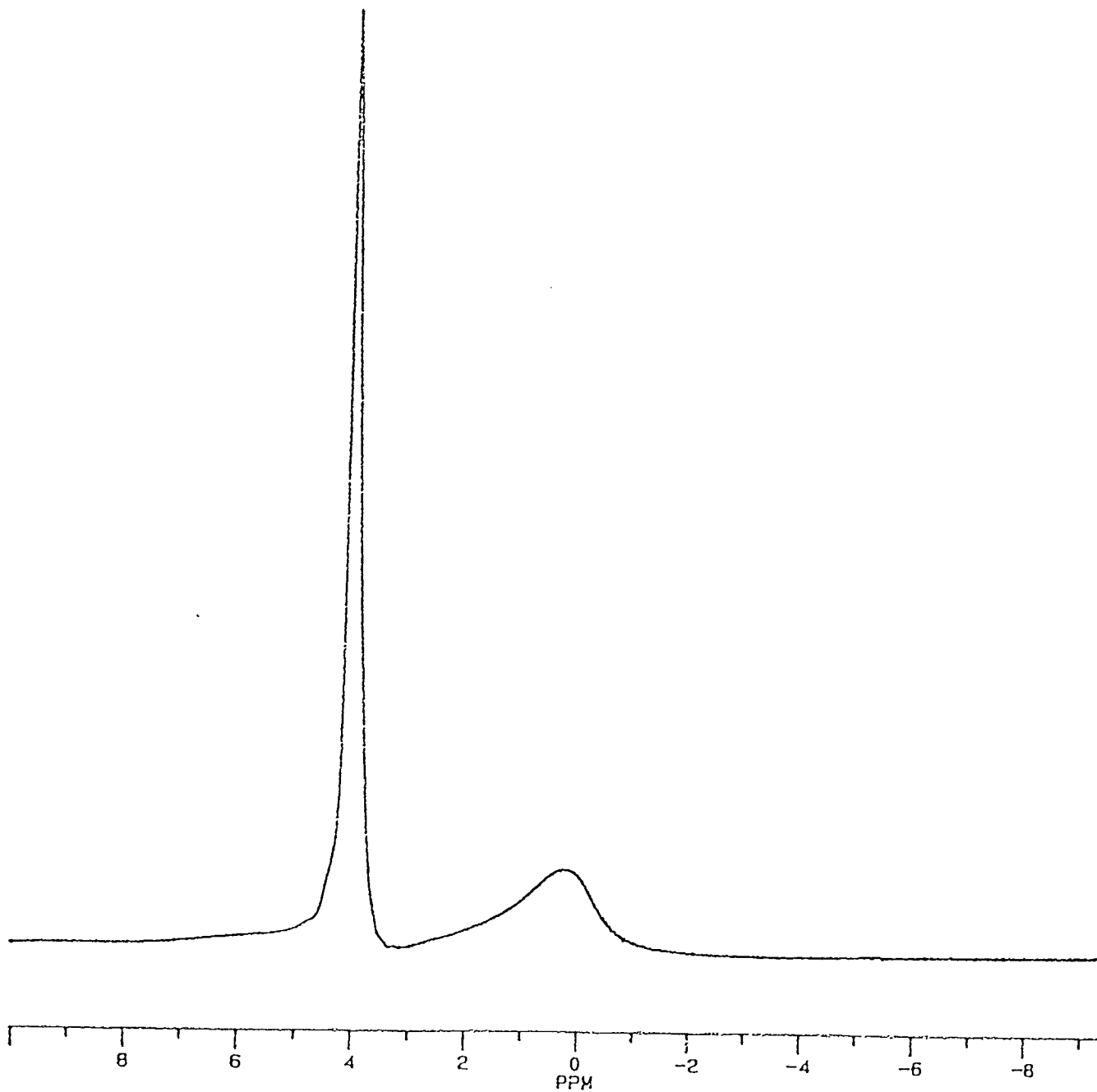
Figure 1 - A 1D NMR spectrum of a UTF fluid

35000   30000   25000   20000   15000   10000   5000
                          HERTZ
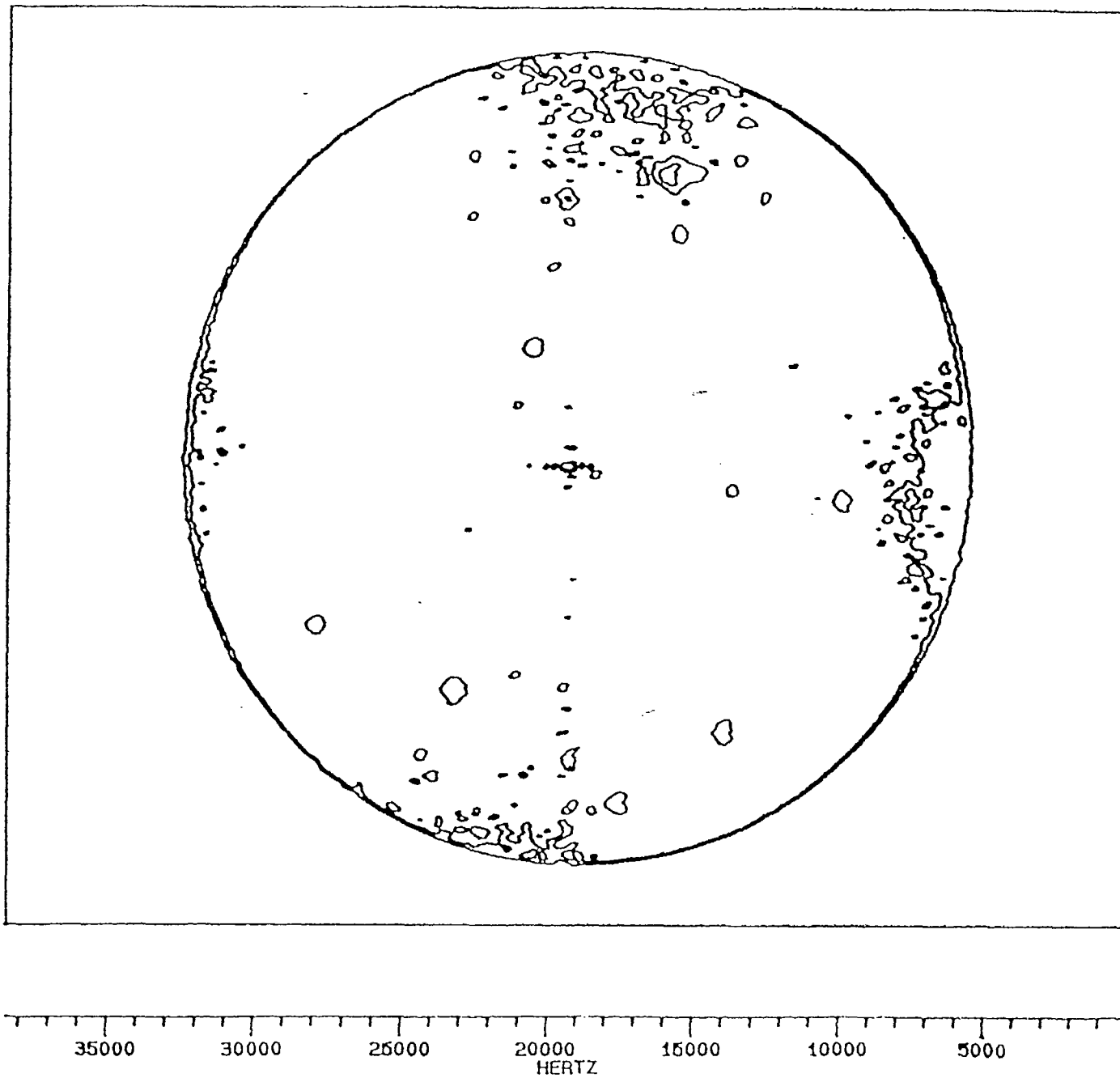
Figure 2 - A spin echo image of a UTF fluid

35000   30000   25000   20000   15000   10000   5000
HERTZ
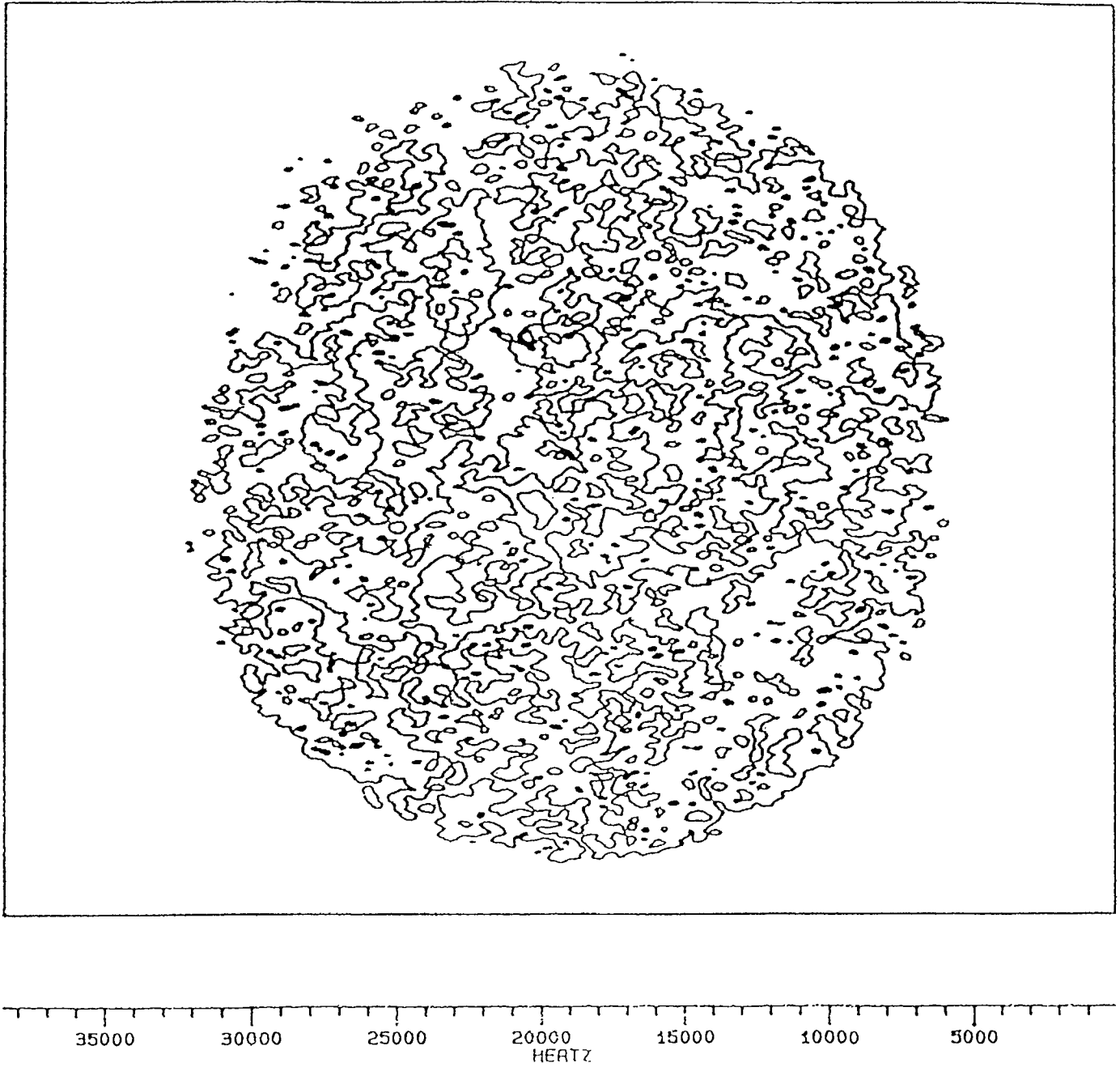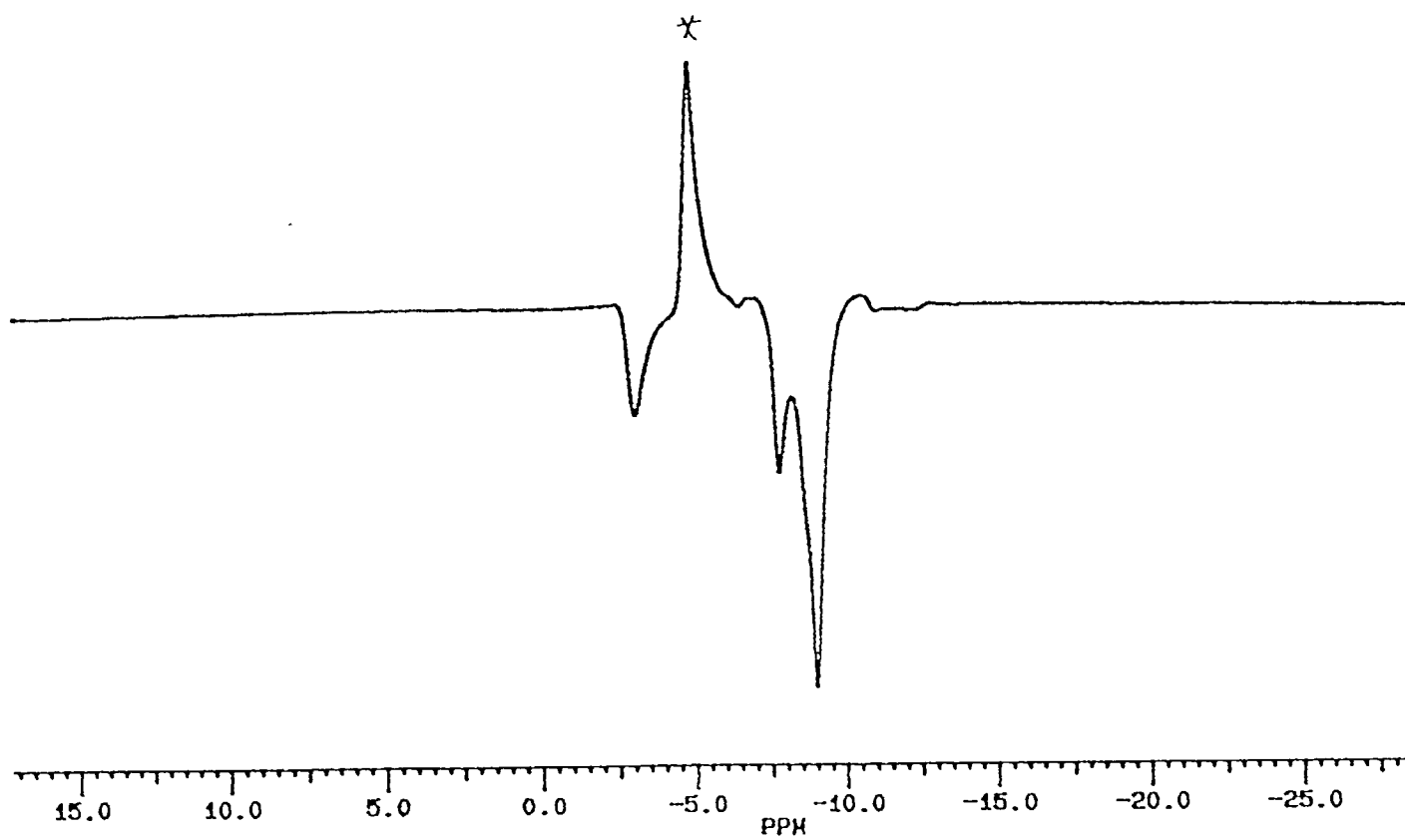
Figure 3 - A spin echo image of froth flotation

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Figure 4 - An inversion recovery ^{1}H NMR spectrum of a
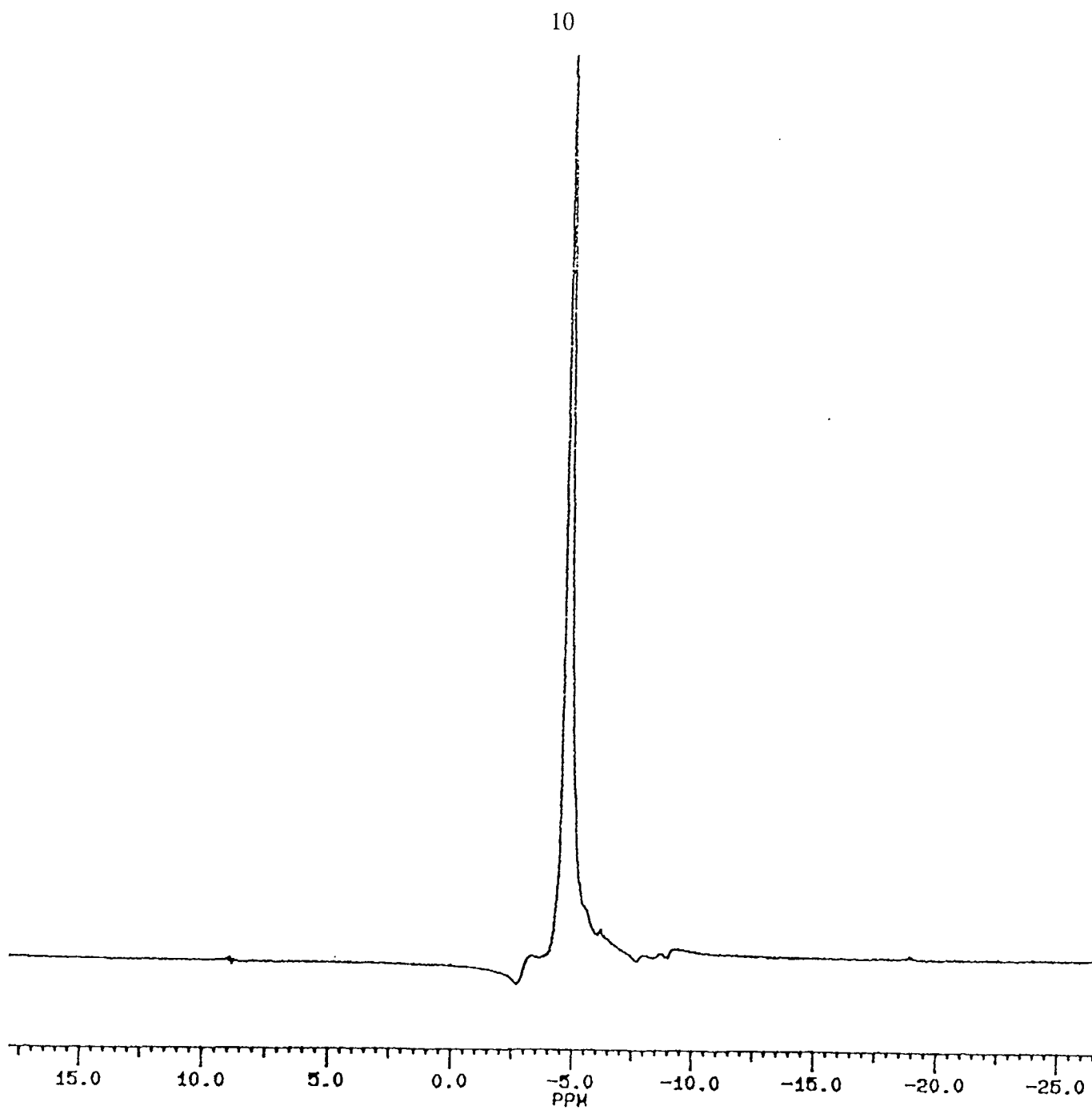gasoline emulsion sample where tau was 300 ms

Figure 5 - A selective ^{1}H NMR spectrum of a gasoline emulsion sample
where the selective pulse length is 6 ms
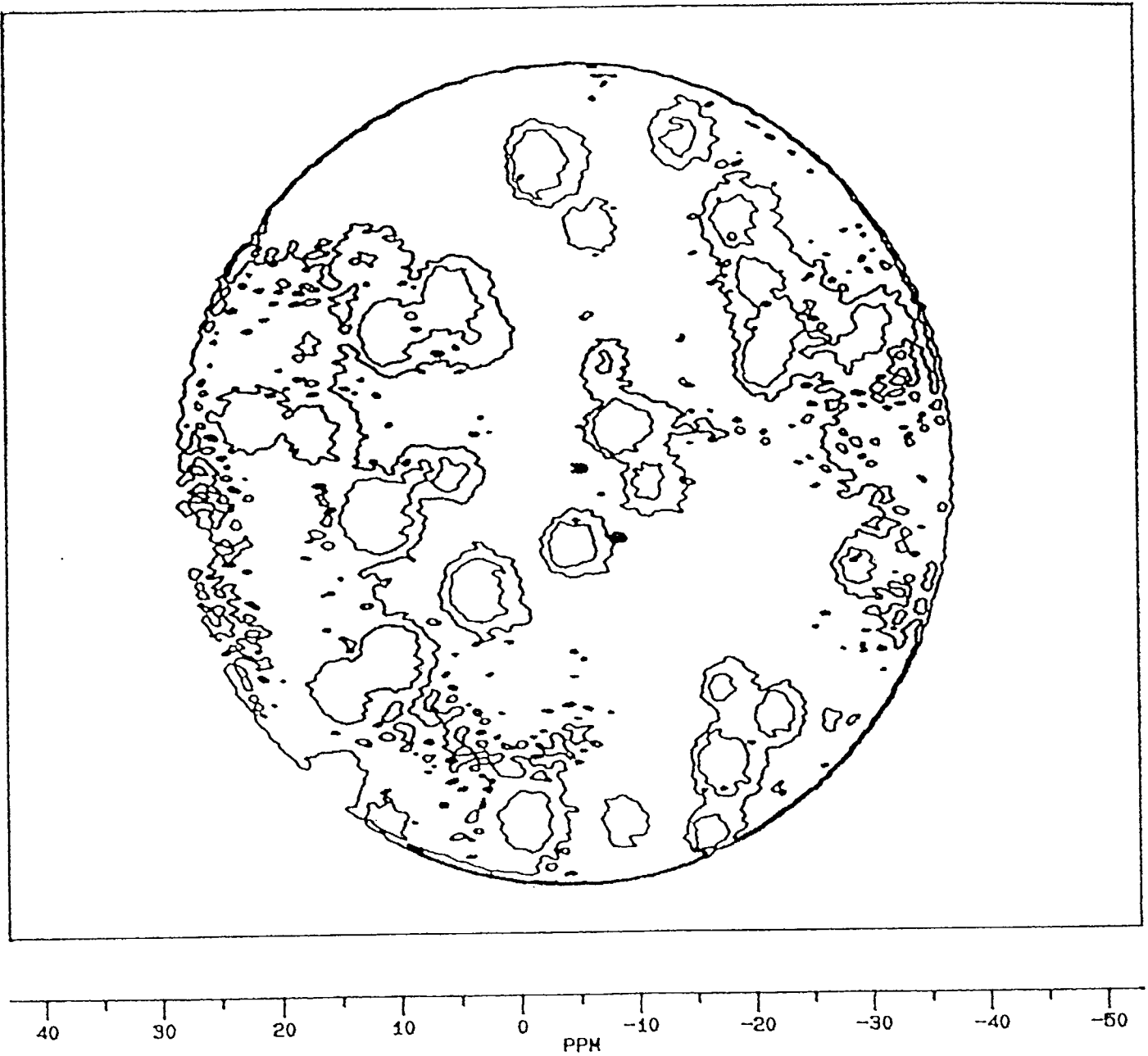
Figure 6 - A chemical selective spin echo image of a gasoline
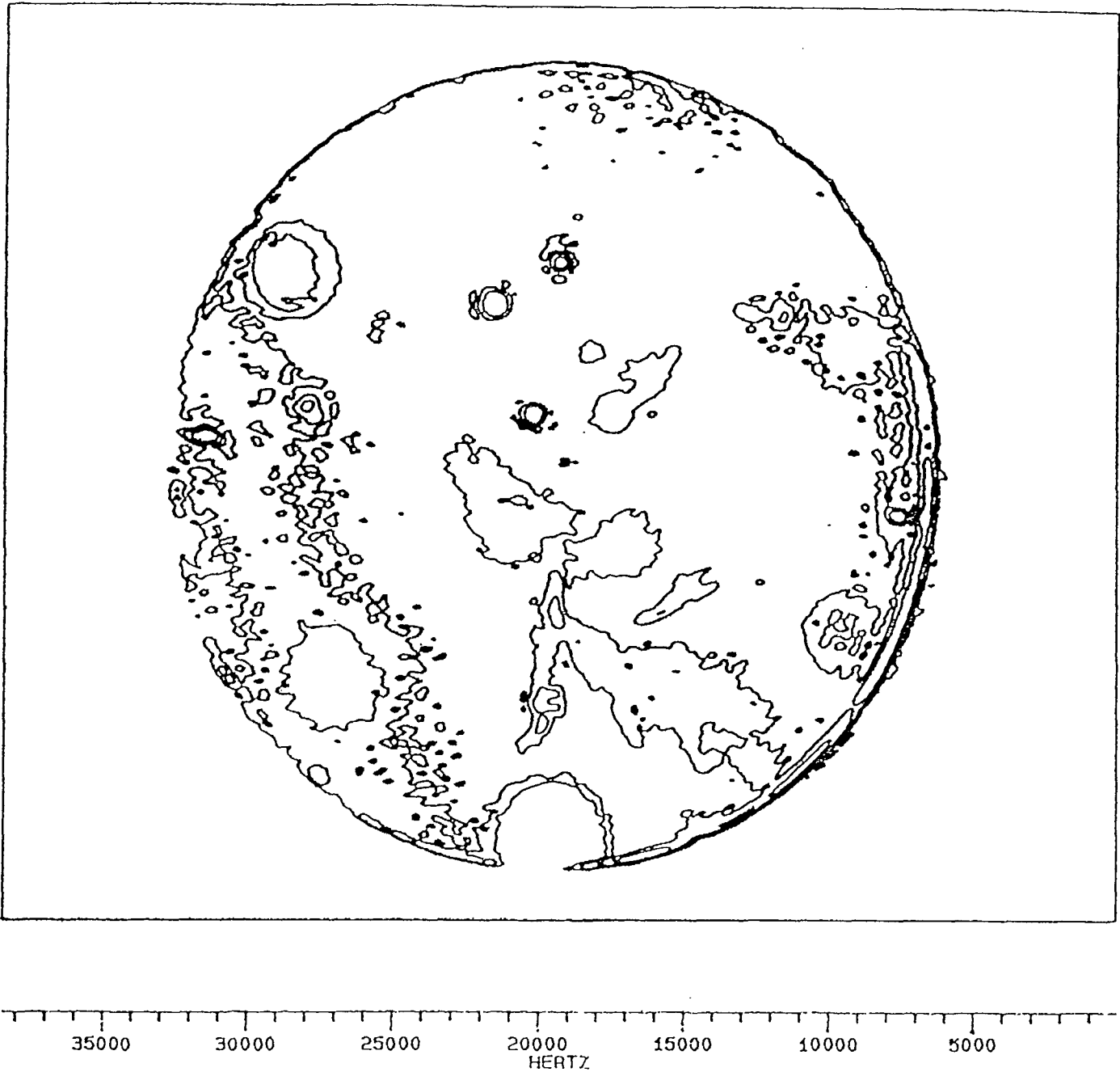emulsion immediately after the sample was shaken into a gel

Figure 7 - A chemical selective spin echo image of a gasoline
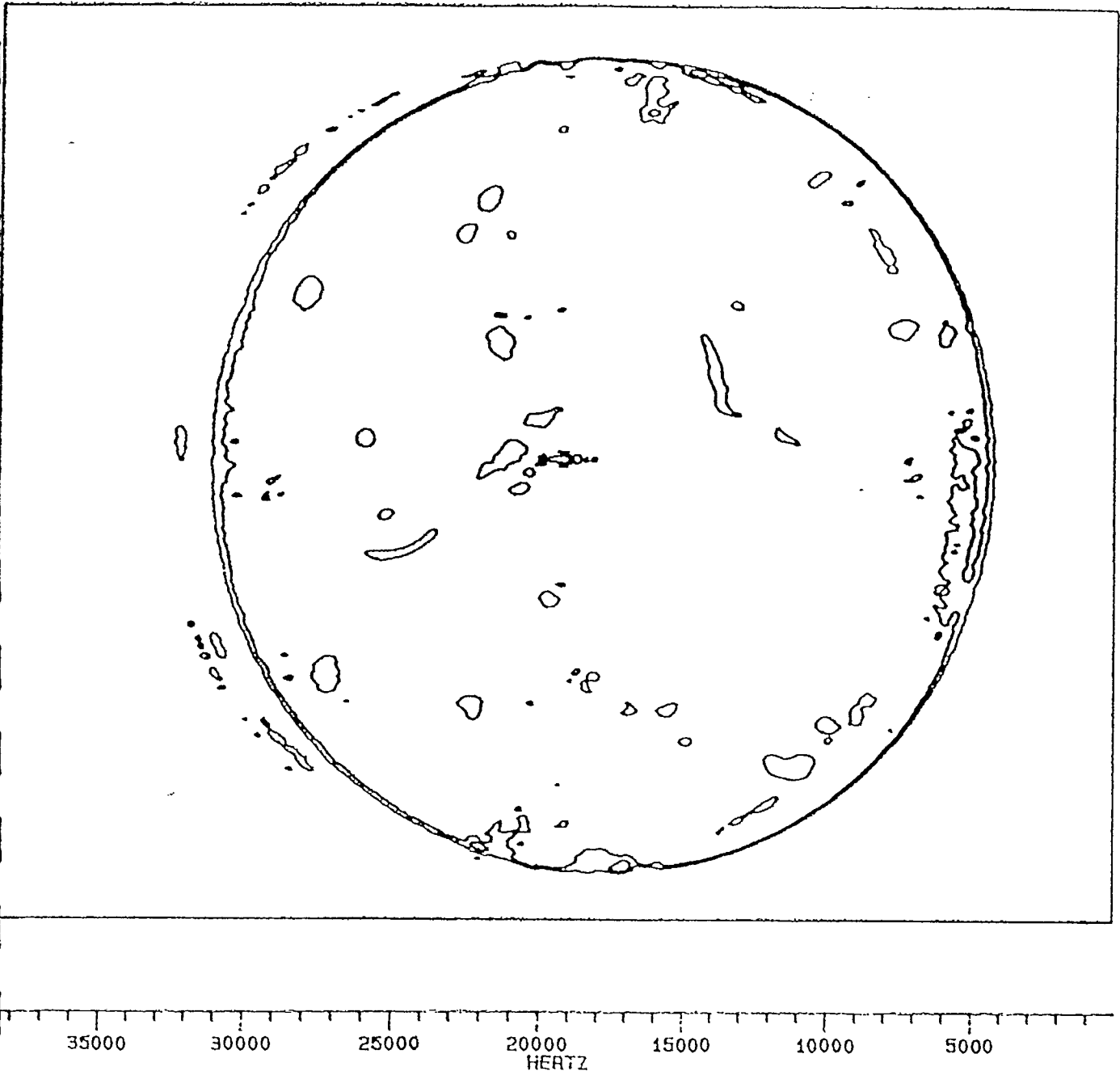emulsion 6 hours after the sample was shaken into a gel

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Figure 8 - A chemical selective spin echo image of a gasoline
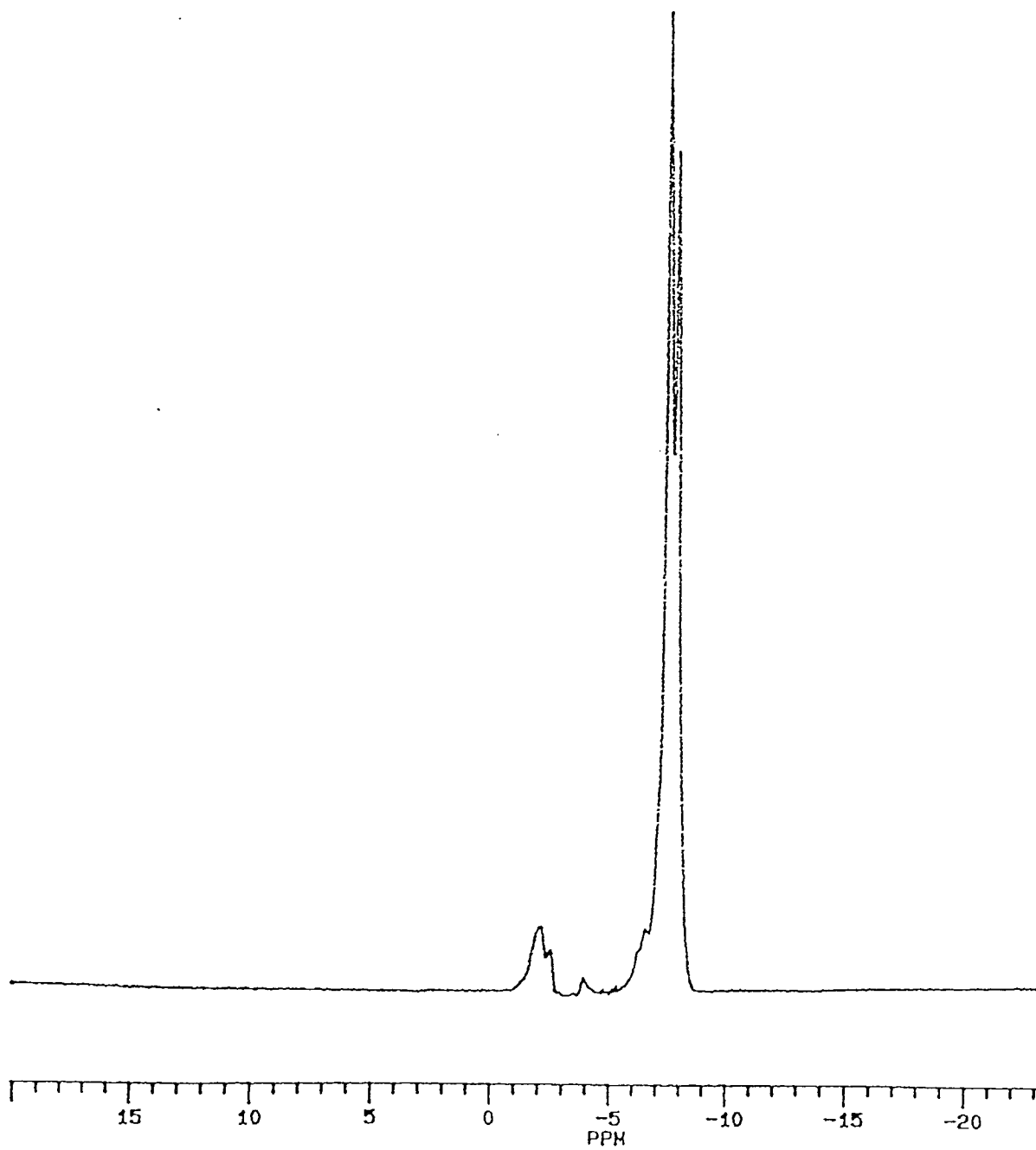emulsion 12 hours after the sample was shaken into a gel

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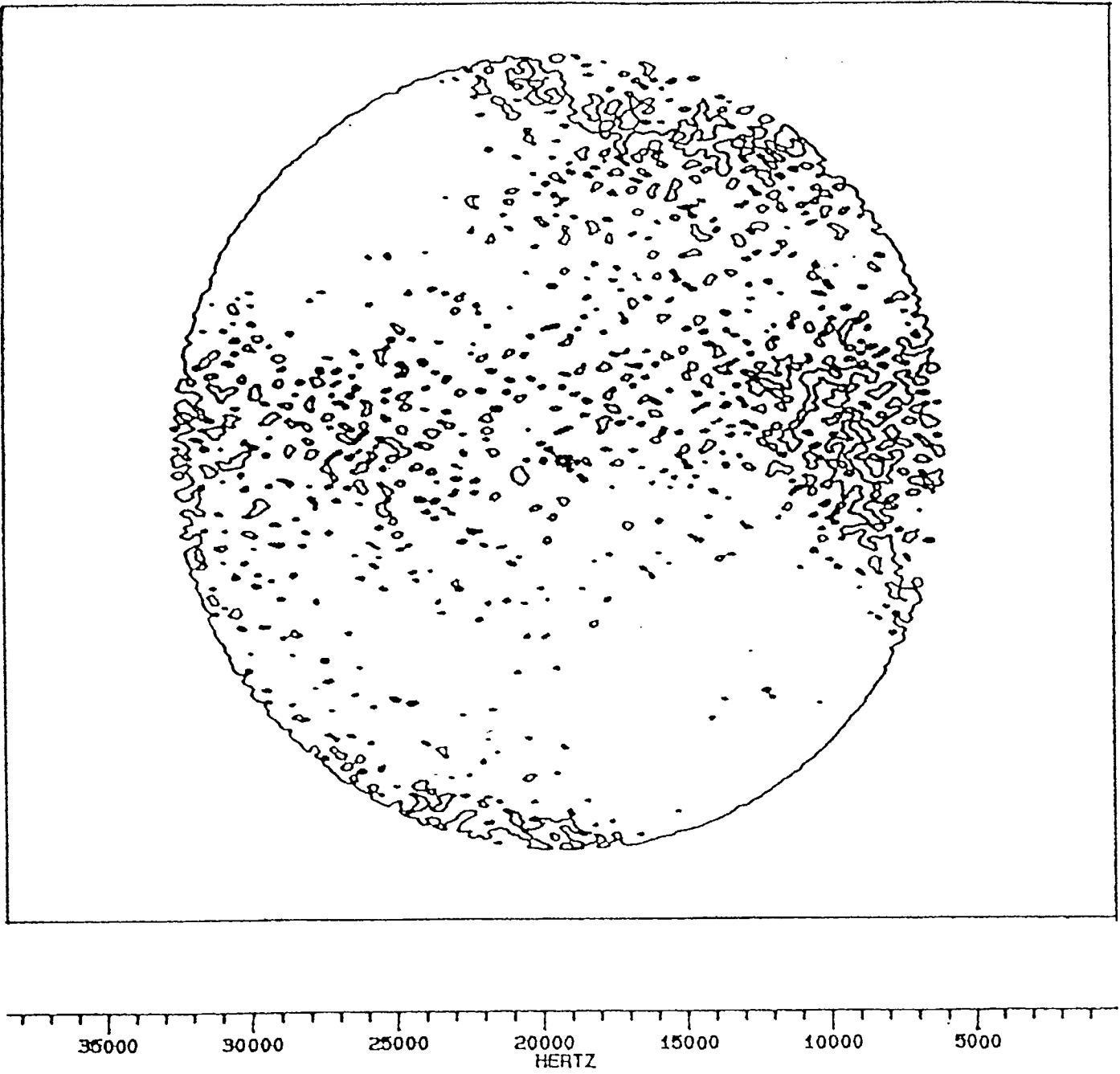Figure 9 - A ^{1}H NMR spectrum of a water in oil sample from the OSLO process

Figure 10 - A spin echo image of a water in oil sample from the OSLO process