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COMPARISON OF GC AND PROTON NMR METHODS FOR THE QUANTITATION OF DIESEL FUEL

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ABSTRACT

The clean up of soils contaminated with petroleum products is associated with several challenges, especially of analytical methodologies. Treatment technologies and site remediation progress will lean heavily on analytical techniques that are accurate, reproducible and of real time value. This paper reports an analytical method for the quantitation of diesel fuel using proton NMR. The method was used to determine the extraction efficiency of the Dean and Stark method, using a sample of waste Diesel Invert Mud. The results have been compared with data obtained from the conventional gas chromatographic method.

INTRODUCTION

Both the design and planning of a soil reclamation program and the evaluation of disposal, reprocessing or reclamation options for sludges, oily wastes and tailings depend upon a reliable and accurate means of evaluating the total oil content of polluted soils. A precise estimate of the amount of hydrocarbons is essential to determine the extent of contamination and the success of the reclamation program.

In our previous work we demonstrated the potential applications of proton NMR in the quantitative determination of bitumen and solvents extracted from oil sands and fine tailings[1-2]. The objective of this study was to explore the application of this technique for the determination of diesel fuel extracted from contaminated soil samples. The proton NMR method has been compared with the conventional gas chromatographic method.

EXPERIMENTAL

Samples. A used Diesel Invert Drilling Mud (DIDM) sample from Alberta, was used for this study. The amount of diesel contained in DIDM was estimated by extraction with toluene using the Dean and Stark Soxhlet method[3]. The extract was characterized and subsequently quantitated by GC. The GC chromatogram of the extract was a good match with the chromatogram of a

sample of diesel obtained from a local gas station in the summer of 1995. This diesel sample was therefore used for preparing calibration standards.

Proton NMR measurements. Proton NMR measurements were performed on a Brucker AM-400 NMR spectrometer (400 MHz); 500 μL of solution in a 5 mm outer diameter tube was used in each case. A repetition time of 2 seconds was selected. Each spectrum was the Fourier transform of 1000 free induction decay curves. Once adjusted all parameters were kept constant for subsequent measurements.

GC determination of diesel. The extract was analyzed employing a Varian Model 3300 GC equipped with an, FID detector and a temperature gradient program. A DB-5, megabore, capillary column, 30 meters in length with a 0.53 mm internal diameter and a 1.5 micron film thickness (J & W Scientific) was used. The initial operating temperature was 50 degrees Celsius with an initial hold-time of 5 minutes. The temperature was then increased at the rate of 10 degrees per minute to a final temperature of 300 degrees Celsius where it was held for 5 minutes. Calibration curves were prepared using the purchased sample of Diesel Fuel #2.

RESULTS AND DISCUSSION

Calibration Curves

Figure 1 shows calibration curves for a diesel sample produced by the gas chromatographic and NMR methods. Both methods gave linear correlations of peak areas with concentration. The correlation coefficients for the first order fit are: 0.9987 for data from GC and 0.9997, 0.989 and 0.9998 for aliphatic, aromatic and total peak areas from proton NMR. This suggests that the two methods will give comparable results. However, the NMR method will have some advantages over the GC-FID method. These advantages are: (1) concentrated samples can be analyzed by NMR without dilution and the overall analysis time will be shorter; (2) interference from naturally occurring substances and ionic and polar species[4] will be less; (3) identification of compounds will be more certain, and (4) the method has the capability to handle high boiling petroleum hydrocarbons.

The limitations of NMR method are: (1) less sensitive than GC, also low precision and long analysis time for concentrations in the ppm range; (2) choice of solvent is very limited, and (3) high instrumentation cost and more specialized personnel training.

Determination of Diesel in a sample of Diesel Invert Drilling Mud

A used Diesel Invert Drilling Mud sample from Alberta was extracted in toluene and carbon tetrachloride using the Dean and Stark Soxhlet method[3]. The extraction was carried out for 20 hours. The extract was quantitatively analyzed by both GC and NMR methods. The results are shown in the following Table:

The Amount of Extractable Diesel in DIDM

Test No.	W/W% of Diesel	
	Determined by GC*	Determined by NMR**
1	6.32	5.93
2	5.83	6.17
3	5.56	6.24
4	-	5.96
Mean	5.90 ± 0.31	6.08 ± 0.13

* Based on the analysis of the toluene extract. ** Based on the analysis of carbon tetrachloride extract.

Considering the reproducibility and the fact that the extractions were carried out in different solvents the results from both methods are not significantly diffent.

CONCLUSION

Proton NMR spectroscopy can be used for the quantitative determination of diesel fuel in non-protonated solvents. The accuracy of this method is comparable to the conventional gas chromatographic method.

REFERENCES

1. Majid, A. and Woods, J. Preprints ACS Div. Fuel Chem. 28, 188-195 (1983).
2. Majid, A. and Sparks, B. D. AOSTRA J Res. 1, 21-29 (1984).
3. Syncrude analytical methods for oil sand and bitumen processing, J. T. Bulmer and J. Star Editors. Alberta oil Sands Information Centre, Edmonton, AB, pp. 46-51 (1979).
4. Fan, C. Krishnamurthy, S. and Chen, C. T., Analysis of soil contaminated with Petroleum Constituents, ASTM STP, 1221, Tracey A. O'Shay and Keith B. Hoddinott,Eds., American Society for Testing and Materials, Philadelphia, 1994.

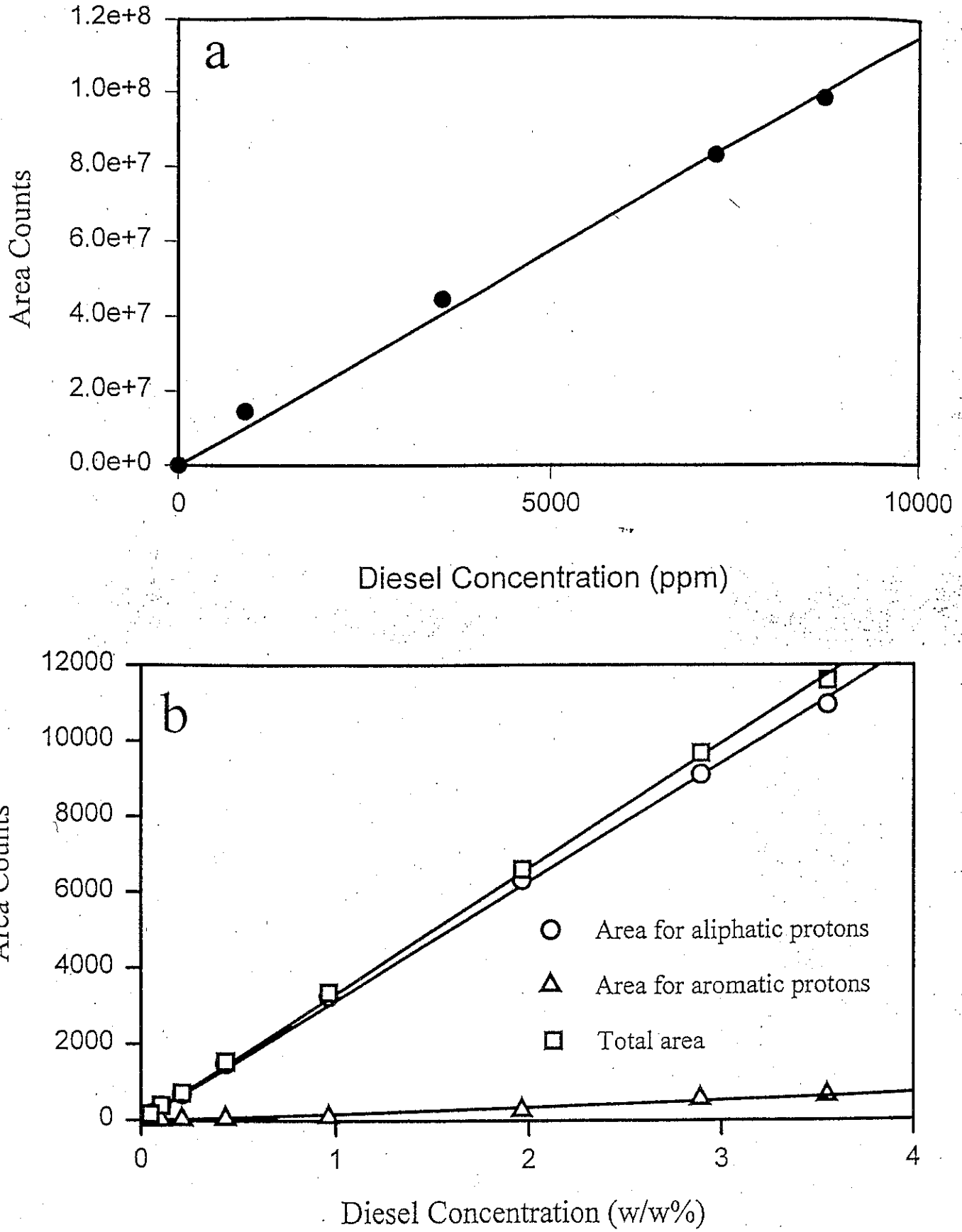

Figure1. Calibration curves for diesel: a). GC b). NMR

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