μ-PIXE Trace Element Analysis of Crude Oil.

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Abstract

Knowledge of trace element concentrations in crude oil has been very useful to the oil industry in the areas of classification and exploration. This paper presents a preliminary study on the analysis of trace elements in crude oil samples using μ-PIXE. The Scanning Proton Microprobe at the University of Oxford was used in study.

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1. Introduction

Petroleum crude contains measurable quantities of trace metals. In addition to the naturally occurring trace elements, other elements are included as additives or picked up as contamination. Knowledge of these traces and the way they are introduced is of some importance to the petroleum industry. When such traces are established to be intimate to crude oil they can be used as a "finger print" of a crude and will indicate its origin. For example the ratio of nickel to vanadium has been used in the characterization of petroleum crude[1].

Crude oil can be contaminated during transportation from the well to the refinery by pipeline material or sea water. It end up containing measurable quantities of nickel, vanadium, sulfur and other undesirable heavy metals. Some undesirable effects associated with these elements have been well documented[2-4]. Nickel and vanadium are deposited on the catalyst during cracking operations adversely affecting the catalyst activity and life. Vanadium in heavy fuel oils is destructive to boilers and turbine components. In addition to nickel and vanadium, iron and copper are known poisons of cracking catalysts.

A number of well established procedures and methodologies have been used to determine trace metals in petroleum crude oils after diluting the sample with an appropriate solvent. Some of these techniques are flame or flame-less atomic absorption spectrometry, X-ray emission spectrometry, X-ray fluorescence spectrometry and charged particle or neutron activation analysis[6-8].

The existing techniques of trace element determination in oil samples rely on some chemical procedures like burning and/or dissolving of samples. These procedures tend to homogenize the sample and may let some of the elements escape from the sample before the measurement takes place. Measurements obtained using the conventional techniques reports data attributed to the whole sample and no information can provided on whether any specific micro phases exist in the sample.

This study is a preliminary work to check whether it is possible to overcome the aforementioned shortcomings in the μ-PIXE technique and using samples in their original form.

2. Experimental Measurements and Results

2. 1 External Beam PIXE Measurement

A set of crude oil samples in original form have been used in this study. The crude oils used varied in type from very light to very heavy. The external beam PIXE method has already been used[9] on crude oil and interesting Ni to V ratios have been reported. A very short run on at the beginning of this study has been conducted using the external PIXE setup at the Nuclear Physics Laboratory, University of Oxford(xx). The samples in this case were oil in its original form trapped behind mylar foils. Before too much time passed all the problems inherent with sample preparation, sample mounting and background were rediscovered. As the major goal of this study is to find the micro-distribution of trace elements in order to find out which traces are intimate to the oil structure, the external beam method will remain limited in providing enough information.

2. 2 μ-Pixe Measurements

The scanning nuclear microprobe at the Nuclear Physics Laboratory, University of Oxford(xx) was used in this work. The first batch of samples were made as thin layers of crude oil on mylar foils. As very small drops of oil are deposited on a mylar foil they spread into a very thin layer. These layers are not uniform in either shape or thickness. Most of the aromatic components of the crude evaporate leaving the saturates along with any other heavier components to be analyzed. Only after most of the volatile components of oil evaporate the samples were placed in vacuum for the actual measurements. Later on a slightly better batch of samples were prepared using drops of oil from samples that have been concentrated by evaporation under medium temperature (50-60 C) for a long time (days).

The μ-PIXE measurements were conducted with a proton beam of 3 MeV. The Si(Li) detector used has effective area of 70 mm2 and it was 20 mm away from the sample. The beam spot size was about 1 μm in diameter. several oil samples have been analyzed. Two dimensional maps showing a few elements of interest have been set up during data acquisition using OM-DAQ the PC-based data acquistion system developed by the Oxford micro-beam group.

2. 3 Results and Discussion

Figure 1 is a two dimensional scan (100 μm long side) showing the distribution of S, Ti, Ca, and Si. Sulfur is well Known to be intimate to

oil and was used in this case to identify the physical limits of the oil layer of the sample. The distribution of Ti was found to be coming mainly from a very small grain-like piece in the sample. The same case was observed for Ca. Si on the other hand has some finer grains of its own. Two X-ray spectra were collected; one was from the whole area of the scan and the other was from a point located on the Ti rich grain. PIXAN program was used to analyze the two spectra and a summary of the major traces is shown in Table 1. Figure 2 shows the distribution of Cl and K in another sample that was found to be rich in Cl. In this case the distribution of both elements follows the same pattern and K can be concluded to have a homogeneous distribution in this sample.

3. Conclusions:

Some of the trace metals found in crude oil are homogeneously distributed in the oil and hence can be considered intimate to the crude. On the other hand trace metals in crude oil can have distributions of their own. In the last case such traces are not intimate to the petroleum. More investigation is needed in this aspect as information of this type is of importance to the oil industry as has been discussed in the introduction.

Acknowledgments

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10.

Figure Captions:

Figure 1

A two dimensional scan of 100 μm long side. It shows the distribution of (starting top left clockwise) S, Ti, Si, and Ca in a crude oil sample

Figure 2

A two dimensional scan of 50 μm long side. It shows the distribution of Cl and K in a crude oil sample.

Table Captions

Table 1

Summary of trace elements found in a crude oil sample. In one case from the whole area of the scan of figure 1, and in the other from a point centered at the Ti rich grain.

Element	Scan Data		Ti Grain Data	
	Concentration	MDL	Concentration	MDL
Mg		44		147
Al	282	23	618	78
Si	254	13	922	54
Sr (L)				
p	37	10	182	47
S	1240	8	1.23%	47
Pb (M)				
Cl	95	6	725	53
K		3	103	32
Ca	129	3	9611	36
Ti	18	3	2.74%	120
Ba (L)	40	7	3.75%	384
V		2		145
Cr		2		89
Mn		1		69
Fe		1	277	38
Co		1		51
Ni	2	1		37
Cu	1	1	141	45
Zn	2	1	136	45
As		2		70
Br		4	62	46
Pb(L)		6	564	104
Sr		7	592	74

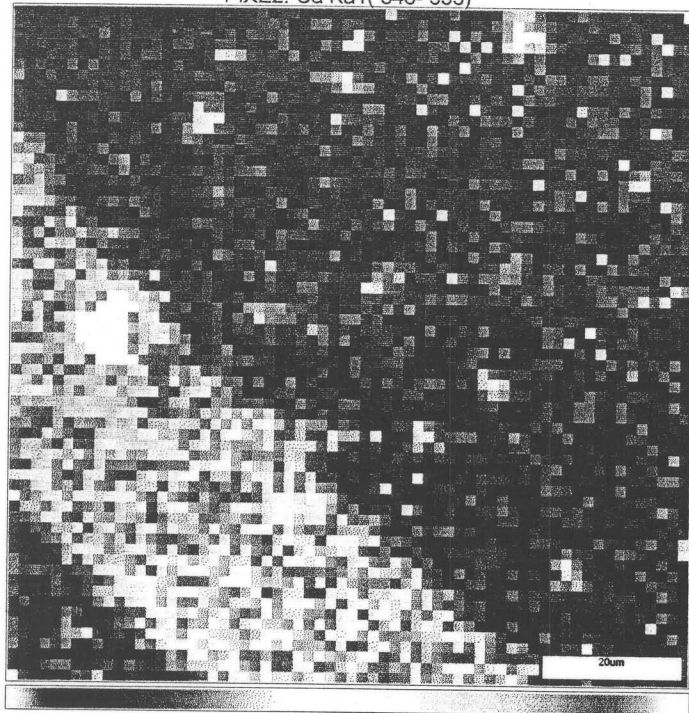# 370037: Crude Oil 1 (100.0 um)

PIXE2: S Ka1(286- 293)
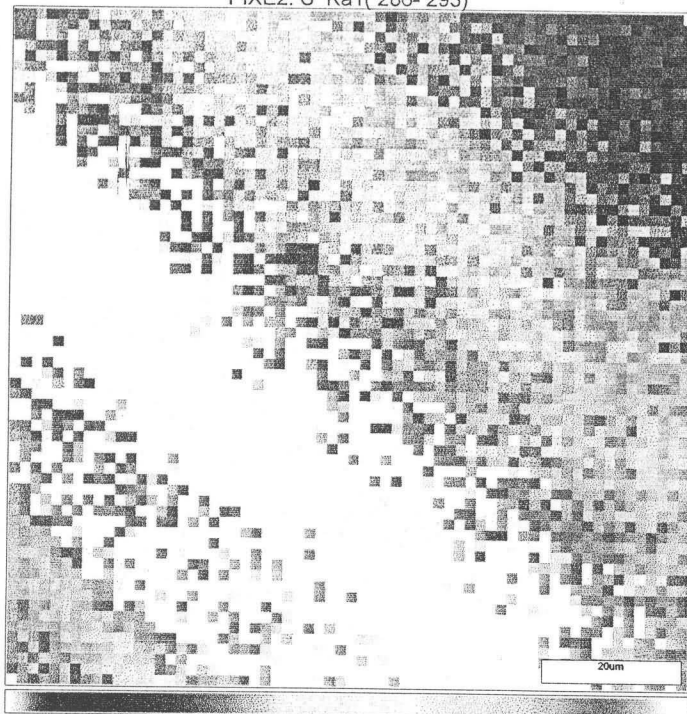
PIXE2: Ti Ka1(382- 392)
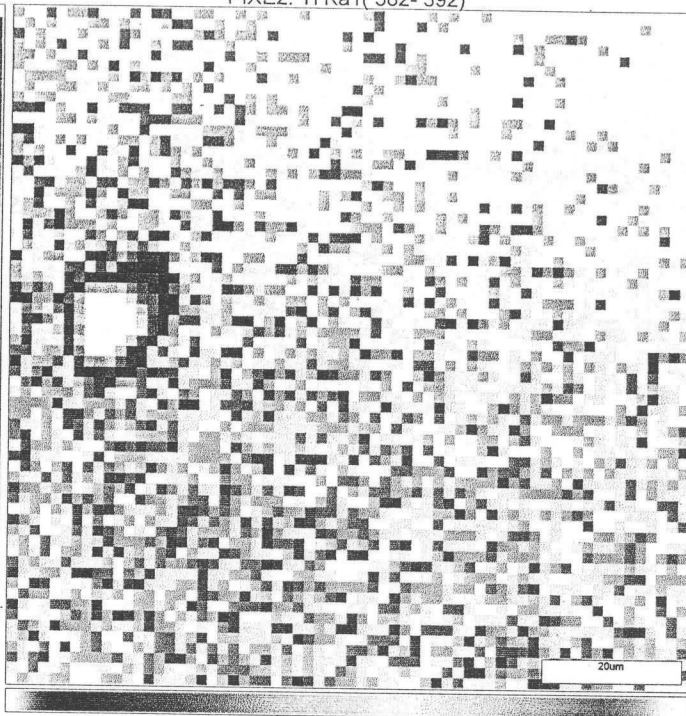
PIXE2: Ca Ka1(346- 355)

PIXE2: Si Ka1(261- 268)

370040: Crude Oil 2 (50.0 um)
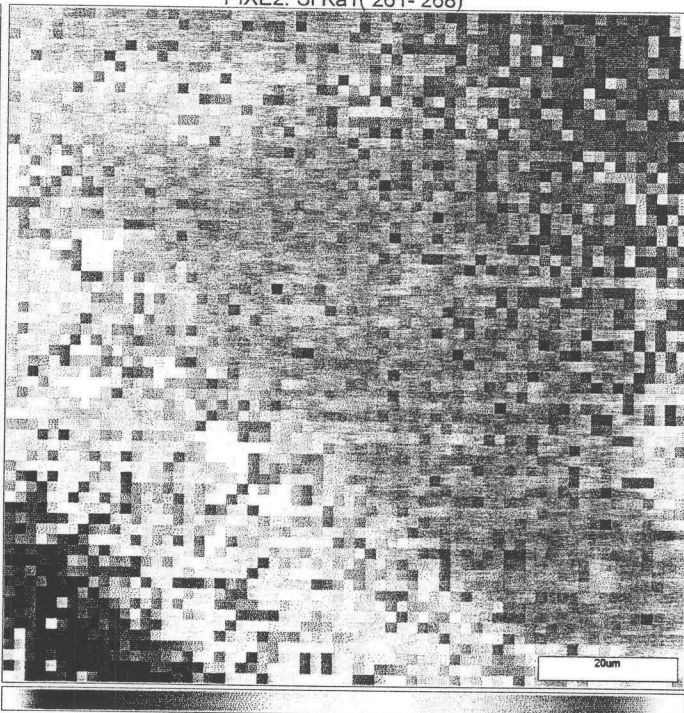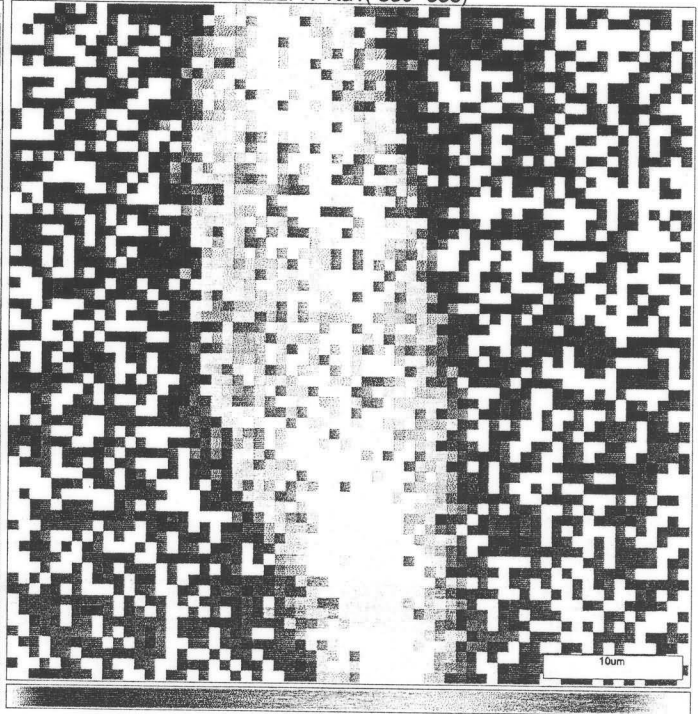

PIXE2: Cl Ka1(300- 307)

PIXE2: K Ka1(330- 338)

10um

10um
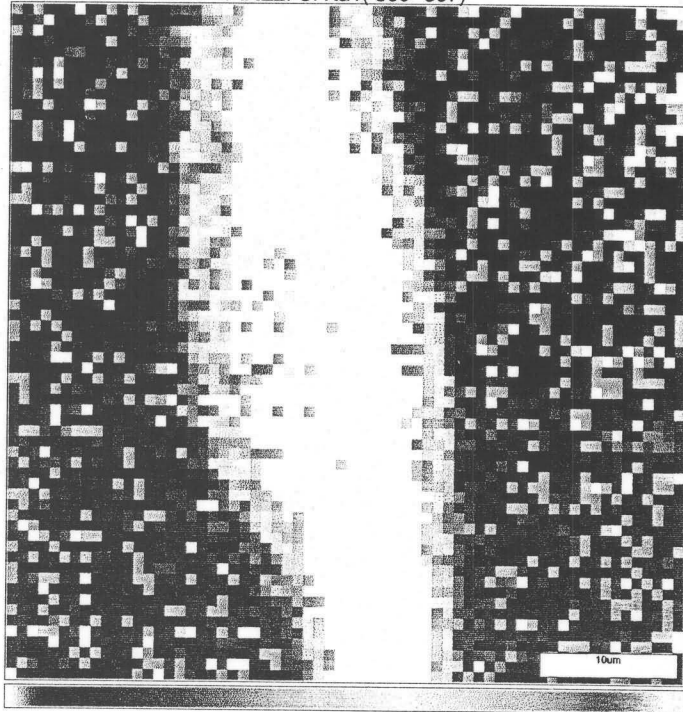
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