

## PTR-MS Mass Spectrometer Detection of Buried Oil

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### Abstract

A novel type of mass spectrometer has been demonstrated to be capable of detecting oils buried in sand by direct sampling in real-time. Tests were first performed using oils placed at the bottom of a larger glass beaker and then systematically covered in sand. Oil samples were then buried on an artificial beach and subsequently detected. The technique has applications to oil detection on beaches and possibly in the arctic environment.

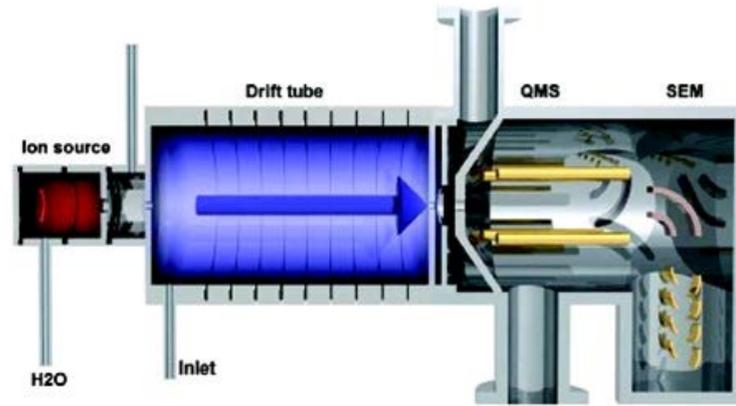
### 1 Introduction

The coast of Brittany in France has seen its share of oil spills and it is not uncommon for ships to be grounded there, leading to the release of both light and heavy oils. A particular problem in this region as elsewhere in the world where there are high tides, is that sand is carried out to sea and back again so that oil that is washed up on a beach one day, is covered in sand the next. Another high tide can expose this oil again later and since this is one of the major holiday regions in France, this represents a major economic as well as an ecological problem. One of the difficulties in this scenario is actually finding the oil on a beach that has seen a spill and where the oil has been covered again by tide driven sand. This has led to a number of techniques being developed and a summary of these methods is given in (API Technical Report, 2014).

In recent demonstration tests performed at CEDRE Research station in Brest (France), a sensitive, transportable PTR-MS Mass Spectrometer apparatus (IONICON QMS300) has been used to detect oil that has been buried in an artificial sand beach. The results of these trials are discussed below.

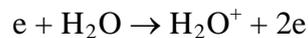
### 2 PTR-MS Mass Spectrometry

The principle of PTR-MS (Lindinger et al. 1998) consists of transferring a proton from the hydronium ion  $\text{H}_3\text{O}^+$  to any species having a proton affinity greater than that of water ( $\text{H}_2\text{O}$ ,  $\text{PA} = 691 \text{ kJ/mol}$ ) (See table I). The protonated species thus created are produced intact, i.e. the molecules are not dissociated, and therefore can be directly identified by their mass. PTR-MS allow measurements to be made in real time of volatile organic compounds such as acetone, acetaldehyde, methanol, ethanol, benzene, toluene, xylene etc., present in the ambient air. The detection limit is on the order of 0.5 ppbv. The linearity of the apparatus generally is maintained up to about 10 ppmv beyond which the apparatus saturates. Its response time is very fast, less than 100 milliseconds.

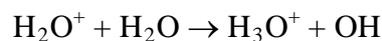


**Figure1. Schematic View of a Proton Transfer Mass Spectrometer (PTR-MS)**

Figure 1 shows the three main sections of the apparatus. The hollow cathode ion source is the part of the spectrometer in which the  $\text{H}_3\text{O}^+$  ions are formed from water vapor. This is possible here using an ion source. This cathode emits electrons which bombard the water molecules:

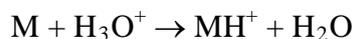


The ions are then injected into a small drift tube, the drift source, where all the newly formed ions react with water to form the ions  $\text{H}_2\text{O}^+$  which, in turn, by reaction with water, form  $\text{H}_3\text{O}^+$  ions according to:



During the transit time in this little drift tube, the rate of conversion of the ions into  $\text{H}_3\text{O}^+$  is greater than 99.5 %. Because of the great purity of primary ions (i.e. in  $\text{H}_3\text{O}^+$ ), it is not necessary to introduce a mass filter between the ion source and the drift tube where the proton transfer reaction will take place.

Once the  $\text{H}_3\text{O}^+$  ions are extracted from the ion source, they are introduced by means of a Venturi type injector, into the drift tube which is continuously filled with the air to analyze. This part is maintained at low pressure (typically 2.2 mbar). All the molecular trace gases  $M$  contained in the air and whose proton affinity is greater than that of water, then receive a proton to form the ion  $\text{MH}^+$  via the reaction:



The ions  $\text{MH}^+$  are then introduced into the detection chamber where they are mass selected using a quadrupole mass filter, then detected by an electron multiplier.

## 2.1 Determination of the Concentration of the Species $M$

Under standard operating conditions, only a small fraction of the  $\text{H}_3\text{O}^+$  ions react with the trace gases,  $M$ . It can easily be established that proton transfer follows the equation:

$$[\text{MH}^+] = [\text{H}_3\text{O}^+]_0(1 - e^{-kt[M]})$$

Where

- $[M]$  is the concentration of the trace gas  $M$  expressed here in molecule. $\text{cm}^{-3}$  ;
- $[\text{MH}^+]$  is the concentration of the protonated trace gas ion;

- $[H_3O^+]_0$  is the initial concentration of the ions  $H_3O^+$  in the absence of  $M$  ;
- $k$  is the rate constant for the proton transfer to the molecule  $M$ . For this type of reaction, its value is generally equal to the so-called Langevin rate, i.e.  $2 \times 10^{-9} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  ;
- $t$  is the mean time that the ions spend in the drift tube, typically  $10^{-4}$  s.

The approximation which is made for the determination of  $[MH^+]$  consists of considering that the concentration of the ions  $H_3O^+$  remains constant during the proton transfer reaction. This hypothesis is justified by the fact that only the molecules having a greater proton affinity than that of water undergo proton transfer. Since all the constituents of ambient air ( $N_2$ ,  $O_2$ , Ar,  $CO_2$ , etc.) have lower proton affinities than water, air acts only as the carrier gas and only the traces gases, present in small quantities in the air, are ionized. Under this condition,  $k \cdot [M] \cdot t \ll 1$  and equation 10 can be simplified, thus:

$$[MH^+] = [H_3O^+]_0(k \cdot t \cdot [M])$$

and this allows us therefore, to determine the concentration of the trace gas

$$[M] = \frac{[MH^+]}{k \cdot t \cdot [H_3O^+]_0}$$

The mass analysis and the detection system of the PTR-MS yield the counting rate  $i(H_3O^+)$  and  $i(MH^+)$ , which are proportional to  $[H_3O^+]_0$  and to  $[MH^+]$  respectively. The mean time  $t$  is calculated from the system parameters (such as drift voltage, pressure, temperature, etc.). As for the rate coefficient,  $k$ , it can easily be obtained from the scientific literature or can be calculated, or even determined experimentally in the laboratory. Knowing all these parameters, the concentration of species  $M$  present in the air can be deduced without calibration.

**Table 1. Proton affinities of several compounds**

Compound	Formula	Molecular Mass	Proton Affinity (kJ/mol)
Argon	Ar	40	369.2
Oxygen	O <sub>2</sub>	32	421
Nitrogen	N <sub>2</sub>	28	493.8
Carbon dioxide	CO <sub>2</sub>	44	540.5
Methane	CH <sub>4</sub>	16	543.5
Ethane	C <sub>2</sub> H <sub>6</sub>	30	596.3
Ethylene	C <sub>2</sub> H <sub>4</sub>	28	680.5
<b>Water</b>	<b>H<sub>2</sub>O</b>	<b>18</b>	<b>691</b>
Hydrogen Sulfide	H <sub>2</sub> S	34	705
Benzene	C <sub>6</sub> H <sub>6</sub>	78	750.4
Propene	C <sub>3</sub> H <sub>6</sub>	42	751.6
Toluene	C <sub>7</sub> H <sub>8</sub>	92	784
O-xylene	C <sub>8</sub> H <sub>10</sub>	106	796
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	58	812

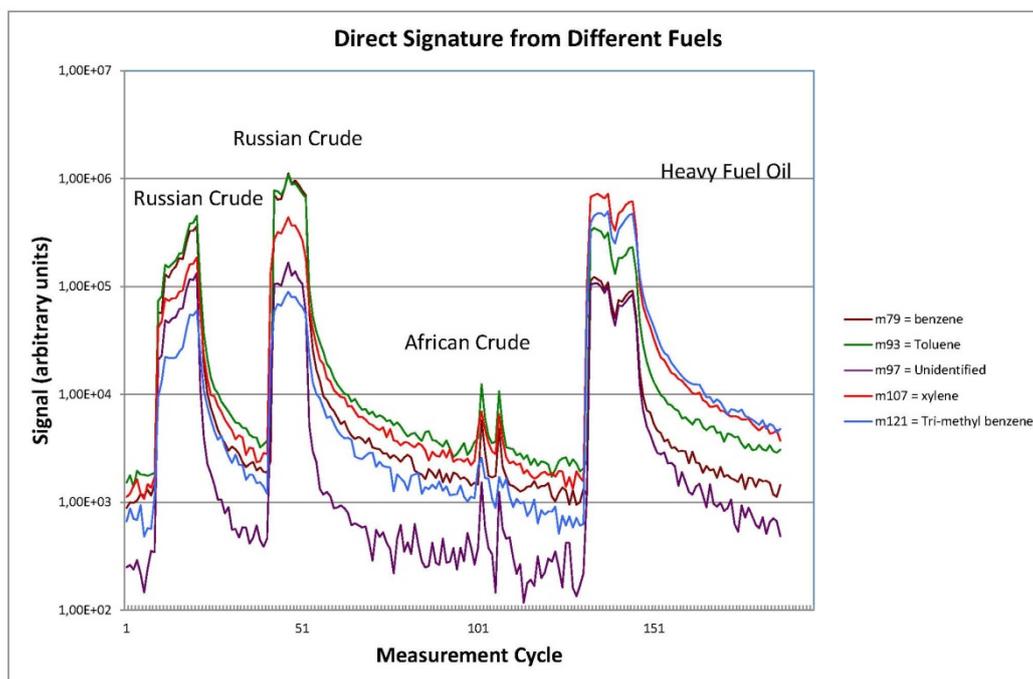
### 3 Oil Detection Measurements

In the introduction, we have introduced the problem of finding buried oil on a sandy beach.



**Figure 2. PTR-MS (Blue Box) Set-up for the Oil Detection Trials on CEDRE's Artificial Beach.**

With the goal of examining the possibility of applying PTR-MS technology to this problem, we have conducted a series of tests at the CEDRE laboratory in Brest, France. As seen in figure, 2, there is an artificial sandy beach which borders a sea-water filled basin. The PTR-MS instrument is the blue box, situated behind its carrying case. The data are recorded on the laptop computer which has dedicated software for acquiring the mass spectra in real time. This can be done, either as by scanning all the masses using repeated sweeps over a pre-defined mass range, or a series of selected masses can be monitored as a function of time. It is the latter mode which was used in the detection experiments, but initially the apparatus was used to identify the principal volatile compounds in two types of crude oil (Russian and African) and a heavy fuel oil. From this initial measurements, it was decided to concentrate on the masses 79, (benzene), 93 (Toluene), 97 (identity uncertain), 107 (xylene) and 121 (tri-methyl benzene) which were the signature compounds for these oils though in differing concentrations. These measurements are shown in figure 3.



**Figure 3. Measurements Taken Directly from the Surface of Uncovered Fuels to Compare Signature Compounds.**

### 3.1 Beaker Tests

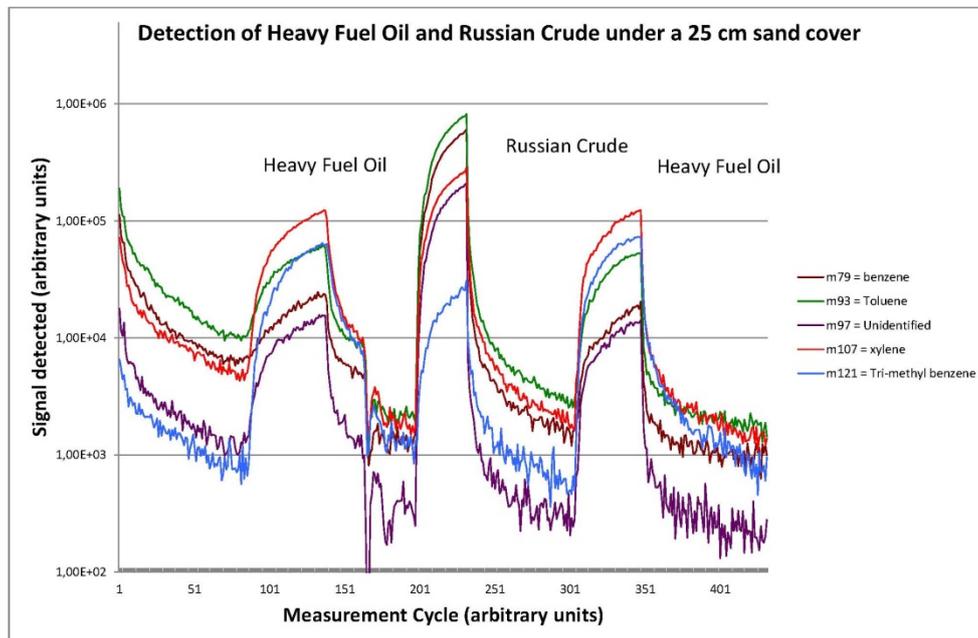
With these initial signatures, a series of tests were then made in which to explore the thickness of sand over an oil deposit through which the underlying oil could still be detected. The measurements consisted on placing about 10 ml of a given oil at the bottom of a large 5L glass flask. The oil was then covered successively with beach sand and the mass scans were taken as the depth of sand cover was increased. In these tests it was found that in each case, the signature compounds could still be detected with a sand cover of 25 cm (10 inches).

The PTR-MS mass spectrometer is able to sample directly from atmospheric pressure and this is done through a, 1.5 m, long, 1.6 mm diameter PEEK tube, maintained at a temperature of 60°C, extended by a 3 meter long, 3mm diameter Teflon tube. This latter tube was fitted at its open end with a glass funnel to increase the collection area and to shield the collection from air currents. Figure 4 shows the set-up for these measurements.



**Figure 4. The Sampling Arrangement for the Oil-in-Sand Beaker Tests**

Figure 5 shows parallel measurements, comparing the compounds detected from the Russian Crude oil and the Heavy Fuel oil. The sampling funnel was placed on the surface of the sand, covering the heavy fuel oil, and it can be seen that the signal quickly rises and falls again when the funnel is removed and placed in an adjacent beaker, containing the sand covered Russian Fuel oil, where this cycle is repeated,. The funnel was returned to the beaker containing the heavy fuel oil.



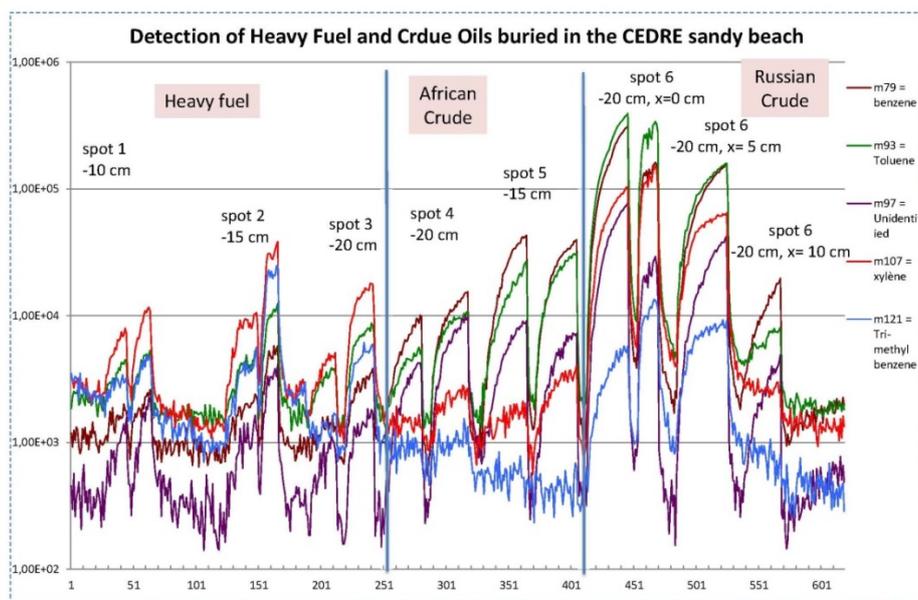
**Figure 5. Sequential Measurements of Signature Compounds from Heavy Fuel Oil and Russian Crude Oil, under 25 cm of Sand.**

It should be noted in figure 5 that the relative concentrations of the signature compounds for these two fuels are quite different. For example toluene is the major signal for the crude oil while xylene is predominant for the heavy fuel oil. Tri-methyl benzene is much more prevalent in the heavy fuel oil than in the Russian crude. It is also noteworthy that the results shown in figure 5 were obtained on the second day of testing, i.e. after the oil had been under the sand for about 24 hours.

### 3.2 Beach Tests

With the experience acquired with the beaker tests, we then proceeded to tests where oil samples were buried at differing depths on the beach itself and then the mass spectrometer was used to verify that the oils could indeed be detected. Again, about 10 ml of oil was used for each spot where the oil was buried. Figure 6 shows some of the results for spots where heavy fuel oil, African crude and Russian crude were buried. The results show the rise (and fall) of the measured signals as the sampling funnel was placed (and then removed) over the spots where the oils were buried. The measurement cycle time was 5 seconds (this depends on the number of masses selected to sample) and the rise time for these peaks was of the order of 20-30 seconds which is linked to the time for accumulating of vapour within the funnel and the transit time through the 3 meter long sampling tube. Where there was more than one peak, this is where the funnel was placed, removed and then replaced and removed at the same spot to check the measurement. In the case of the Russian crude oil, the three peaks represent measurements where the funnel was first placed over the burial spot, then displaced by 20 cm (its diameter), and then again by a second displacement of 20 cm. The object of this measurement was to have some insight into the radius of sensitivity of the technique. This is illustrated in figure 7.

Again it should be noted that not only was the oil detected in each case but the compositions of the spectra were seen to be different indicating the product sensitivity of the technique.



**Figure 6. Detections of Buried Oils at Different Spots on the Beach**



**Figure 7. The Sampling Funnel, displaced by 40 cm from the Burial Site for the Oil Sample (First Ring)**

#### **4 Summary and Discussion**

Both light crude and heavy fuel oils were used in these trials and it was found that these oils could be detected while being covered by up to 10 inches of sand. Furthermore, the mass spectral signature of the oils being different, we could distinguish between the different oil types used (refined or crude oil). These tests were not designed to search for buried oil in unidentified locations. They were intended purely as proof-of-principle measurements and as such it must be said that the results were very encouraging. The very high sensitivity of the measurement technique indicates that it can be used to detect even small quantities of buried oil. This technique may even be able to detect weathered oils for in one brief test, some (unidentified) dry tar-balls found on the artificial beach, were buried under a few inches of sand and their presence could be detected by the instrument.

Further tests are planned to explore the potential of the method for sandy beaches and also in ice conditions. These will be more systematic and obviously it will be of interest to do blind survey measurements to ascertain if it is feasible to use this technique as a practical *in operando* oil detection method.

#### **5 References**

Lindinger, W., A. Hansel, and A. Jordan, "On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS): Medical applications, food control and environmental research", Review paper, *Int. J. Mass Spectrom. Ion Proc.*, 173: 191-241, 1998.

*Subsurface Oil Detection and Delineation in Shoreline Sediments*, API Technical Report 1149-2A, October 2014.