

Scientific paper

# Laundering of “Illegal” Fuels – a Forensic Chemistry Perspective

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## Abstract

Samples of dark-red liquids with acidic sediments, and petroleum odour were examined. Analyses using automated thermal desorption followed by gas chromatography – mass spectrometry (ATD-GC/MS), scanning electron microscopy coupled with an energy dispersive X-ray spectrometer (SEM-EDX) and X-ray fluorescence spectrometry (XRF), allowed us to conclude that the samples were probably residues of an illegal activity involving the removal of Solvent Yellow 124 from heating gas oil. The aim of the present work is to illustrate the application of common analytical procedures used in forensic laboratories for analysis of complex samples, and aided by expert knowledge in problem solving.

**Keywords:** illegal fuels, forensic sciences, ATD-GC/MS, SEM-EDX, XRF, Solvent Yellow 124

## 1. Introduction

Samples of dark-red liquids with sediments which had been collected from barrels at an illegal storage place were delivered for examination. The liquids were acidic (pH 1–3) had a petroleum odour. The questions of interest from public prosecution were:

1. What is the content?
2. What is the source (e.g. a technological process) of these samples?

The identification of organic and inorganic compounds in complex matrices (unknown evidence samples) is a common task in forensic examination. The samples had a strong aroma of petroleum products, thus they were analysed for presence of petroleum derived compounds by gas chromatography (GC).

Due to the acidity of the liquids it was not advisable to inject them directly to GC. Static headspace analysis with passive adsorption on Tenax TA was used, which is efficient for isolation and preconcentration.<sup>1</sup> The so obtained sample can be analysed by gas chromatography – mass spectrometry. This procedure has been satisfactorily applied to detection of petroleum products and organic solvents in samples of fire debris and other samples with complex matrices as well.<sup>2–5</sup> The sediments associated with these samples were analysed by scanning electron microscopy coupled with an energy dispersive X-ray spectrometer (SEM-EDX), which is used for elemental analysis of various samples in forensic laboratories.<sup>6</sup> As

SEM-EDX method only provides information about major and minor elements (> 0.1 wt%), X-ray fluorescence spectrometry (XRF) was employed to determine the contents of trace elements.<sup>7</sup> A drawback of XRF is that elements with  $Z > 11$  are not detected. Nevertheless, a combination of SEM-EDX and XRF provided the information on qualitative and semi-quantitative elemental content of sediments present in the samples. Further analyses were used to determine the identity of acids.

## 2. Experimental

### 2.1. Chemical Analysis

pH and the presence of nitrate was indicated by the used of indicator papers (Merck). The presence of chloride was tested using concentrated  $\text{NH}_3(\text{aq})$  and additionally, using  $\text{AgNO}_3$ . The presence of sulphate was tested using  $\text{BaCl}_2$ .

### 2.2. ATD-GC-MS Analysis

For qualitative analysis, a few drops of each liquid were placed in separate closed glass jars with 3 adsorption tubes (Supelco) filled by Tenax TA (polyoxide 2,6-diphenyl-*p*-phenylene). Then they were heated at 60 °C for 4 h. Thermodesorption was performed using ATD Turbo Matrix (Perkin Elmer) at 335 °C for 20 min and

concentrated on a cold-trap ( $-30\text{ }^{\circ}\text{C}$ ) with Tenax TA. The compounds were thermodesorbed with a heating speed  $40\text{ }^{\circ}\text{C s}^{-1}$  up to  $335\text{ }^{\circ}\text{C}$ , and maintained at this temperature for 20 min. The gas chromatograph (Auto System XL, Perkin Elmer Instruments; column: Rtx-5Sil MS  $30\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$ ; Restek) with a mass spectrometer (TurboMass, Perkin Elmer) was used for identification of analytes. The temperature programme was:  $30\text{ }^{\circ}\text{C}$  maintained for 3 min; increase  $5\text{ }^{\circ}\text{C min}^{-1}$  to  $120\text{ }^{\circ}\text{C}$ , increase  $15\text{ }^{\circ}\text{C min}^{-1}$  to  $270\text{ }^{\circ}\text{C}$ ;  $270\text{ }^{\circ}\text{C}$  maintained for 7.5 min.  $\text{EI}^+$  ionization ( $70\text{ eV}$ ) was used and the ions were detected in the range  $35\text{--}350\text{ m/z}$ . The Willey Registry of Mass Spectral Data 2000, Mass Spectral Browser v. 3.2.1 and LIB2NIST v. 1.0.0.5 libraries were used for identification.

### 2.3. SEM-EDX Analysis

Wet sediments from each sample were mixed with acetone (pure p.a., Polskie Odczynniki Chemiczne) to remove the organic compounds by sonication (Sonic-2, Polsonic) for 10 min and centrifugation ( $12,000\text{ rpm}$  for 2 min; Centrifuge 5414D, Eppendorf AG.). After decantation, the solid phases were air-dried and placed on self-adhesive carbon discs (TAAB) on an aluminium stub (TAAB) used with Scanning Electron Microscope JSM-5800 (Jeol). After that they were carbon coated using an SCD sputter (Bal-Tech, Switzerland). The prepared stub was mounted in the sample chamber of SEM coupled with an energy dispersive X-ray spectrometer (Link ISIS 300, Oxford Instruments). A qualitative elemental analysis of the sediments was carried out using an accelerating voltage of  $20\text{ kV}$ , a life-time of  $50\text{ s}$ , and a magnification of  $500\times$ .

### 2.4. XRF Analysis

Another part of each of the prepared sediments was placed in a sample cup (Chemplex Industries) and analysed by X-ray fluorescence spectrometer EDX2000 (Oxford Instruments). The analysis was made in a helium atmosphere. A lamp with silver cathode was used as a source of X-ray (accelerating voltage  $25\text{ kV}$ ), which allowed the detection of K-series lines from sodium to molybdenum, and L-series lines from rhodium to uranium where the duration of analysis was  $60\text{ s}$ .

## 3. Results

### 3.1. Chemical Analysis

The chemical analyses indicated chloride ions in the headspace. Analysis of aqueous phase indicated the presence of chloride and sulphate ions. Nitrate was not present in a detectable amount.

### 3.2. ATD-GC-MS Analysis

The analyses of the samples, made under the described conditions, enabled the detection of mixtures of *n*-alkenes (with  $> 8$  atoms of carbon) in each sample. The obtained chromatograms (Figure 1) were compared with chromatograms present in databases of flammable liquids and petroleum products made during previous experiments.<sup>3–5</sup> The search indicated that this composition was characteristic of diesel fuel and/or heating gas oil. An interesting observation was that a peak and mass spectrum,

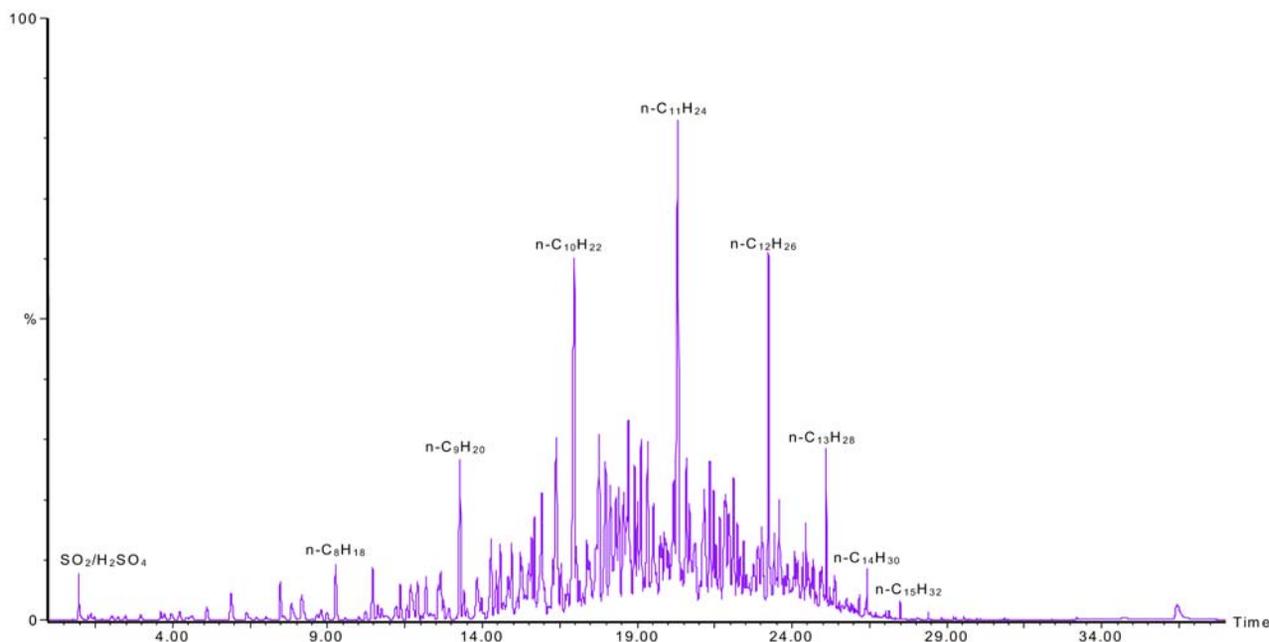


Figure 1. A chromatogram of sample analysed by ATD-GC/MS method.

characteristic of sulphur dioxide and/or sulphuric acid, were found on the chromatograms of each analysed sample. The presence of sulphuric ions was also confirmed by chemical tests.

### 3.3. SEM-EDX Analysis

The results from qualitative analysis by SEM-EDX method are presented in Figure 2. Oxygen, magnesium, aluminium and silica were detected in the samples and comprise the main elemental composition of the sediments from the evidence samples at a detection level of 0.1 wt.%. The presence of carbon was explained by the carbon coating on each sample.

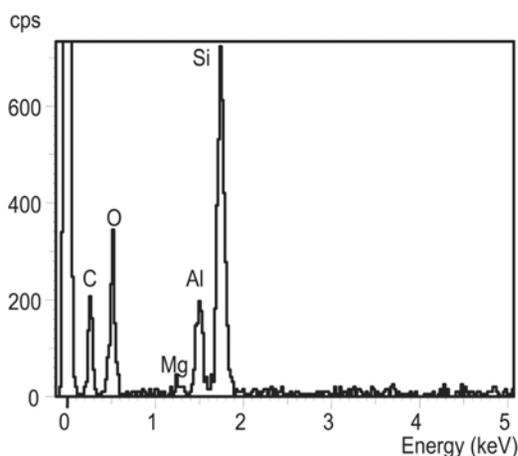


Figure 2. A SEM-EDX spectrum of dried sediments.

### 3.4. XRF Analysis

The XRF analysis also detected the presence of calcium, sulphur, titanium, manganese and iron (Figure 3).

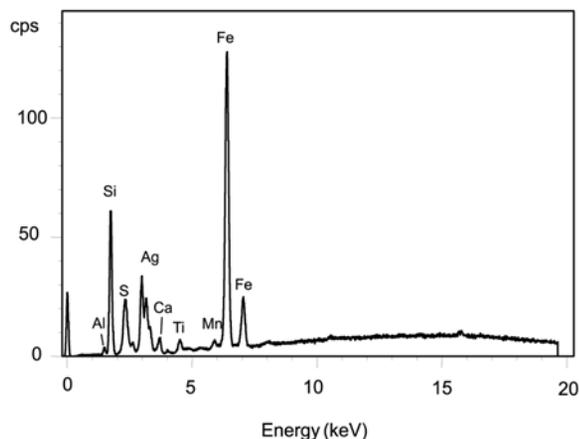


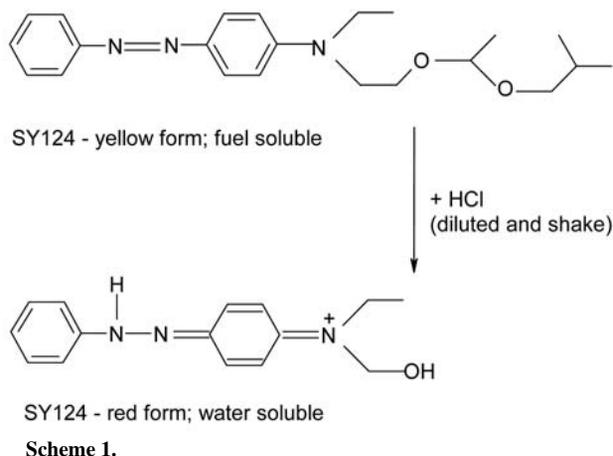
Figure 3. Sediment analysis by X-ray Fluorescence Spectrometry.

## 4. Discussion

An answer to the question of the prosecution – What is the content of the evidence liquids? – had to be answered based on the performed analysis. It was evident that these samples contained diesel fuel and/or heating gas oil, hydrochloric acid, and had a dark-red colour because they contained residues of the Solvent Yellow 124 dye as a consequence of its removal (i.e. “laundering”) from heating gas oil to make illegal vehicle fuel. The explanation of how the last conclusion was obtained is presented in the next paragraphs.

Oils may be used for different purposes and taxed at different rates. Diesel fuel for vehicles may find its use also as heating oil, in which case it is sold at a much lower price. The dye called Solvent Yellow 124 (also named SY124, Sudan 455, Somalia, Euromarker) is prescribed by law within the European Union after August 2002 to distinguish between fuel used in diesel engines (without SY124) and cheaper fuel for heating purposes (with SY124)<sup>8</sup>. These two liquids have almost the same composition and either could be used in vehicle engines. However, oil for heating purposes can also contain more than diesel fuel, which in extreme cases can result in damage to diesel engines. Nevertheless, there is a financial incentive to misuse heating gas oil as diesel fuel because of different taxation. The objective of criminal activity is to buy heating gas oil, remove the dye and sell this fuel as ‘uncoloured’ diesel fuel. The illegal profit could be hundreds of millions of euro per year.

SY124 (Scheme 1) is a yellow azo dye (*N*-ethyl-*N*-[2-(isobutoxyethoxy)ethyl](4-phenylazophenyl)amine). SY124 is added in amounts of ca. 6 mg/L<sup>-1</sup>. If fuel containing Solvent Yellow 124 is shaken with HCl, the yellow neutral molecule soluble in fuel transforms into a bright red product, which is water soluble.



The acetal group, which provides good solubility in a non-polar liquid (e.g. diesel fuel), is lost by hydrolysis when shaken with an acid, which also helps the transfer of

the dye from the fuel to the aqueous phase. The dye can be concentrated by using a small volume of acid to extract it from a large volume of fuel. We conclude that the sample sediments were most probably the remains of hygroscopic material used for removal of traces of water from the fuel following the extraction.

The most reasonable explanation of a possible source of sulphur dioxide, and/or sulphuric acid, could be that these compounds were a by-product of a reaction of sulphur-containing compounds (e.g. organic compounds which are part of heating gas oil and/or diesel fuel) and the hydrochloric acid used to concentrate SY124.

## 5. Conclusions

The results of analysis showed that dark-red evidence sample liquids were mixtures of hydrochloric and sulphuric acid, and of *n*-alkenes (with at least 8–15 atoms of carbon per particle). The chromatogram obtained by ATD-GC/MS was characteristic of diesel fuel and/or heating gas oils. Moreover, the analysis of sediments performed using SEM-EDX and XRF methods, showed that they contained mainly oxygen, magnesium, aluminium, silica and calcium. This suggested that the samples could have originated from the process of illegal removal (“laundering”) of the Solvent Yellow 124 dye out of heating gas oil in an attempt to produce “illegal” vehicle fuel oil.

High performance liquid chromatography<sup>9</sup> is used to determine Solvent Yellow 124 in heating oils, but can only be applied to unchanged oils. The application of this

technique to the samples described in this paper is not straightforward. This research is continued.

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## 7. References

1. R. Borusiewicz, *Probl. Forensic Sci.* **2002**, *L*, 44–63.
2. G. Zadora, J. Zięba-Palus, R. Borusiewicz, *Probl. Forensic Sci.*, **2002**, *LII*, 124–132.
3. R. Borusiewicz, G. Zadora, J. Zieba-Palus, *Chromatographia* **2004**, *60*, S133–S142.
4. G. Zadora, R. Borusiewicz, J. Zieba-Palus, *J. Sep. Sci.* **2005**, *28*, 1467–1475.
5. R. Borusiewicz, J. Zięba-Palus, G. Zadora, *Forensic Sci. Int.* **2006**, *160*, 115–126.
6. G. Zadora, Z. Brożek-Mucha, *Mater. Chem. Phys.* **2003**, *81*, 345–348.
7. T. Hicks, F. Monard Sermier, T. Goldmann, A. Brunelle, C. Champod, P. Margot, *Forensic Sci. Int.* **2003**, *137*, 107–118.
8. D. McCallien, Fighting fuel fraud with solvent dyes, [http://www.sdc.org.uk/general/features/feature\\_fuel.htm](http://www.sdc.org.uk/general/features/feature_fuel.htm) (accessed: 20 March 2006).
9. S. Hendericsson, R. Westerholm, *J. Chromatogr. A* **1996**, *723*, 395–398.

## Povzetek

Analizirali smo forenzične vzorce temno rdeče tekočine vonja po petroleju, z usedlino. Uporabili smo termično desorpcijo, ki ji je sledila plinska kromatografija z masno spektrometrično detekcijo (ATD-GC/MS), elektronsko mikroskopijsko z energijsko disperznim spektrometrom (SEM-EDX) in rendgensko fluorescenčno spektrometrijo (XRF). Z uporabo ekspertnega znanja pri interpretaciji analiz kompleksnih vzorcev smo ugotovili, da gre za ostanke nelegalnega odstranjevanja barvila Solvent Yellow 124 iz kurilnega olja.