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Use of GC/FT-IR/MS in the analysis of aircraft deicing fluids

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IRD Application Brief

HP 5965B IRD
HP 5971A MSD

IRD 93-3

IRD productivity profile

Industry
Environmental

Chemicals
Glycols

Analysis
Identification of components
Quantitation of components

Abstract

The use of combined GC/IRD/MSD is shown to be highly useful in the qualitative and quantitative analysis of aircraft deicing/anti-icing fluids. Library searching of the components and impurities as well as quantitation is demonstrated.

Introduction

Aircraft deicing/anti-icing fluids (ADAF) are commonly used to remove ice, snow, and frost from commercial, military, and private aircraft. These fluids are usually glycol based solutions. In North America, most ADAF formulations consist largely of ethylene glycol (EG), diethylene glycol (DEG), and propylene glycol (PG). Although the exact percentage of the glycols will depend on the specific formulation, these ADAF fluids are generally composed of 34 to 90% EG with 8 to 44.5% water. ADAF fluids may also contain a variety of other agents, such as dyes, corrosion inhibitors, and preservatives.

It has been estimated that Canada uses approximately 8 million liters of ADAF and the United States another 44 million liters in a typical year. In Canada, this represents as much as 5800 tons of glycols used in airport deicing/anti-icing operations. Since very few airports have a formal mechanism of recovering ADAF fluids, much of this fluid is released directly into the environment, usually through airport drainage systems. [1]

Because ADAF fluids contain glycols as a relatively high percentage of their formulation, monitoring programs have focused on the detection of

glycols as a method to determine the fate and effect of ADAF fluids in the environment. In particular, glycols are known to indirectly affect aquatic organisms by contributing to an increased biochemical oxygen demand (BOD) of water.

The extreme water solubility of glycols makes these compounds very difficult to extract. For this reason, analytical techniques have focused on direct injection of aqueous samples into gas chromatographs equipped with flame ionization detectors. This method requires the use of 0.53 mm columns with a film thickness of at least 1 μm. GC-FID methods generally have detection limits in the range of 5 mg/l which is well below the Canadian guideline level of 100 mg/l of total glycols.

Although GC-FID methods have detection limits sufficient to meet the guidelines, ADAF fluids may contain various glycol isomers which would be difficult to identify and impossible to confirm using the FID. For this reason, a method of analysis which provides structural information is desired. GC/FT-IR and GC/MS are two methods which can provide this type of information and have sufficient detection limits. Their combined operation also provides high confidence qualitative identifications. In order to evaluate these selective detection systems, spiked water samples and actual field samples were analyzed.

Results

In order to successfully chromatograph these polar glycols in aqueous solution not only was an HP-FFAP column required but the IRD flow cell needed modification. The normal KBr windows were replaced with water impervious ZnSe ones. The IRD and MSD were operated in the parallel configuration with a 10 to 1 post column split favoring the IRD. Details of this are found elsewhere. [2]

Illustrated in Figure 1 are the chromatographic and spectral data for a 100 ppm standard of the three ADAF components. The infrared and mass spectra of ethylene glycol are shown.

Figure 2 shows IR and MS data, both chromatographic and spectral, of the ADAF II deicing fluid. Even with the sample diluted 1000 to 1 with water for chromatographic analysis about 5 nanograms of acetic acid was detected by the IRD and 0.5 nanograms by the MSD.

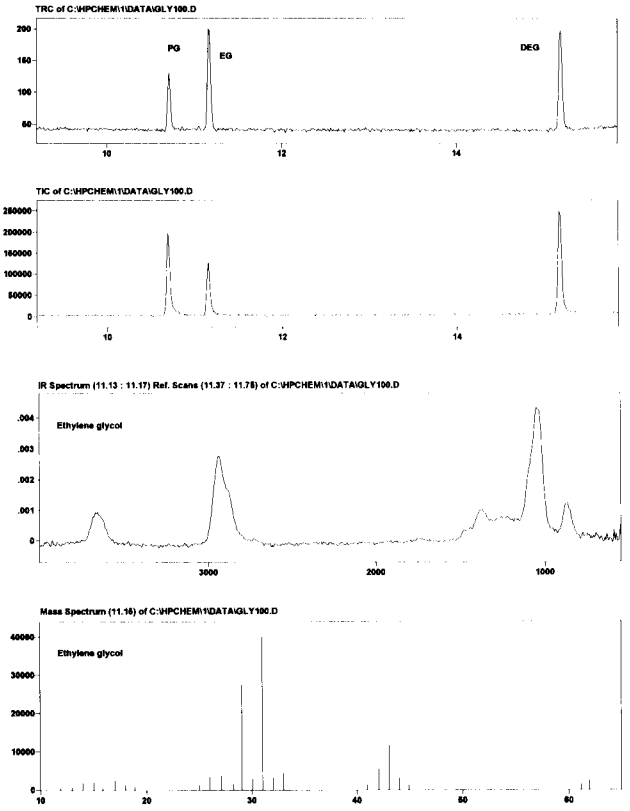

Figure 1. Combined GC/IRD and GC/MSD output of propylene glycol (PG), ethylene glycol (EG), and diethylene glycol (DEG) standards at the 100 ppm level with IR and Mass spectra of EG shown.

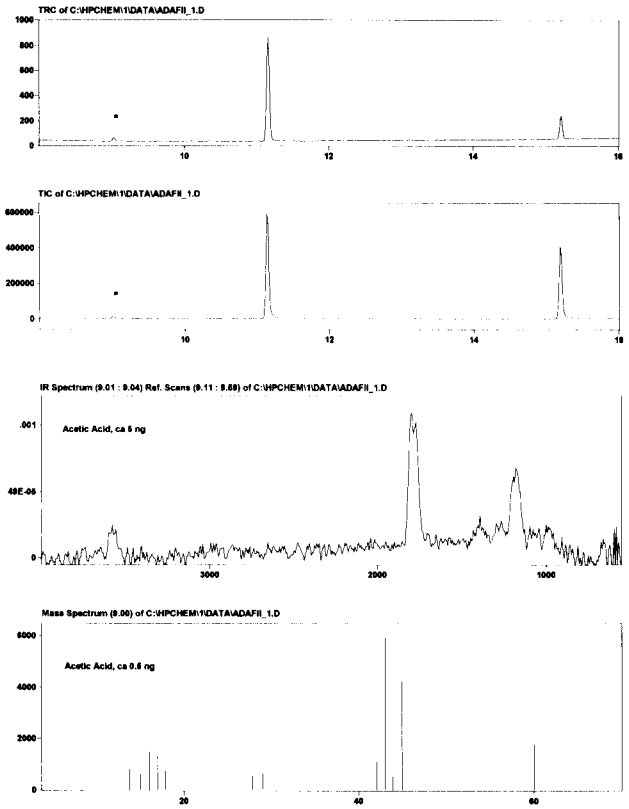

Figure 2. Combined GC/IRD and GC/MSD output of aircraft deicing/anti-icing fluid ADAF II diluted 1000 to 1 with IR and Mass spectra of acetic acid shown.

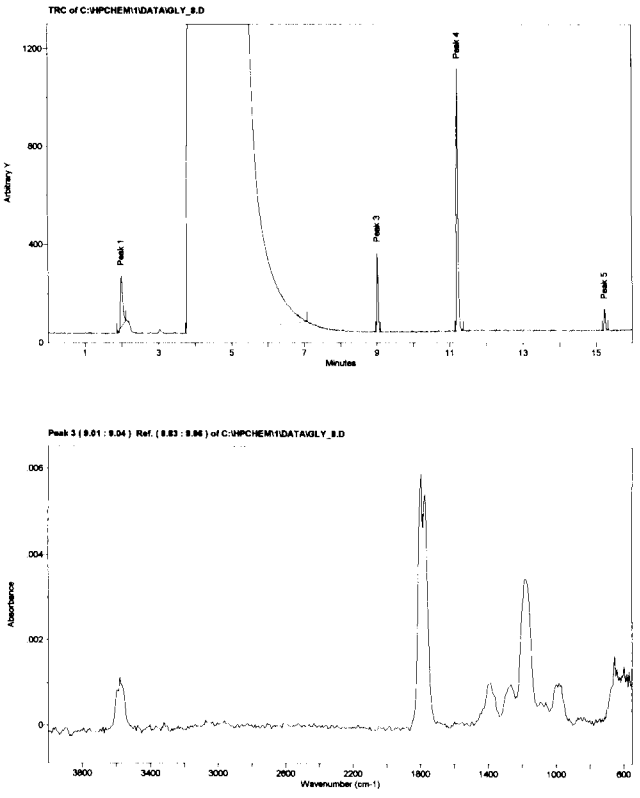

Figure 3. IRD total response chromatogram of GLY_8, an airport grab sample, and infrared spectrum of acetic acid.

Significant amounts of acetic acid are found in the GLY_8 airport runway grab sample, see Figure 3. Spectral quality is good and correct library searches are possible, see Figure 4.

Quantitation of these glycols and their impurities can also be done. Figure 5 shows the calibration curves for the three glycols. From this calibration the ethylene glycol level in GLY_8 is calculated to be approximately 630 ppm. Similar quantitation could be done using MS data.

```
Information from Data File:
File        : C:\HPCHEM\1\DATA\GLY_8.D
Operator    : Roger Leibrand
Acquired    :  4 Mar 93   2:17 pm using AcqMethod GLYCOL
Sample Name: Environment Canada Samp 8 Gylcol Grab
Misc Info   : 30M .53MM 1uM HP-FFAP 60-220@10 He 70kPa
Vial Number: 1

Search Libraries:   C:\DATABASE\WILEY.L              Minimum Quality:  80
                    C:\DATABASE\NBS75K.L             Minimum Quality:   0

Unknown Spectrum:   Apex
Integration Params: AutoIntegrate

Pk#  RT    Area%        Library/ID                    Ref#     CAS#    Qual
-----------------------------------------------------------------------------
  1   9.01   8.32 C:\DATABASE\WILEY.L
                  Acetic acid                       113851 000064-19-7 90
                  Acetic acid                       113855 000064-19-7 83
                  Acetic acid                       113853 000064-19-7 78
IR3   9.02       C:\DATABASE\IRD\ALDRICH.LIB
                  ACETIC ACID, 99.8%                  1699 000064-19-7 .2181
                  C:\DATABASE\IRD\EPA_REVA.LIB
                  ACETIC ACID, 99.8%                   485 000064-19-7 .2327
                  C:\DATABASE\IRD\FLAV_IR.LIB
                  ACETIC ACIDD, 99.8%                  831 000064-19-7 .2362
```

Figure 4. Combined IR and MS library search results for acetic acid

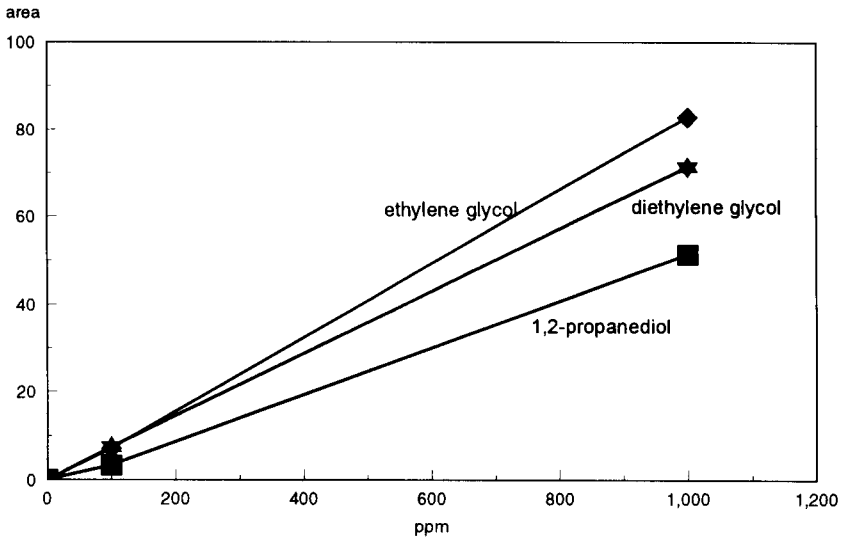

Figure 5. Calibration curve for ADAF glycols

Conclusion

Combined GC/IRD/MSD analysis of aircraft deicing/anti-icing fluids was performed to identify the components present and to quantitate a sample of airport runoff.

References

1. Environment Canada (Conservation and Protection), Transport Canada (Airports Group), Proceedings: Aircraft Deicing and the Environment, July 6–9, 1992, Montreal, Quebec, Canada

2. Leibrand, R. J. and Duncan, W. P., *Investigation of the Chromatographic Optimization of Combined GC/FTIR/MS,* Int. Lab. 46–52 July (1989)

Conditions

Gas Chromatograph

Column: 30 m × 0.53 mm × 1 µm film of HP-FFAP
Carrier Gas: Helium at 70 kPa
Oven: 60 °C to 220 °C at 10 °C/min with 5 min hold
Injection Port: 250 °C
Sample Injection: 1 µl, splitless

IRD parameters

Light pipe: 270 °C
Transfer lines: 300 °C
Sweep Gas: Nitrogen at 35 kPa inlet, 100 kPa outlet
Scan Parameters: 8 cm^{-1} resolution, 4 coads, 1.5 scans/second stored
Detector: Wide Band MCT, 550 to 4000 cm^{-1}
Flow Cell Windows: ZnSe

MSD parameters

Mass Range: 10 to 310 daltons
Scan Parameters: 3 A/D samples, 1.4 scans/second stored

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