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DETERMINATION OF GLYCOL IN AIRCRAFT GROUND DEICING/ANTI-ICING FLUIDS USING FLOW INJECTION WITH REFRACTIVE INDEX DETECTION

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Summary—A simple method for determining glycol in deicing/anti-icing fluids has been developed. The method uses a single line FIA system with detection based on Schlieren optics. The concentration range was 0–5% glycol and the limit of detection was 0.05%. Samples were preferably pumped at a flow rate of 0.7 ml/min and 100 μl of distilled water was injected (reverse FIA). Detection was accomplished with an 18 μl spectrophotometric flow cell at a wavelength of 410 nm. The conduit connecting the injector and the detector was 10 cm long and had an inner diameter of 0.5 mm. The traditional FIA approach can also be applied, *i.e.* injection of samples into a carrier of water, but the linear working range is narrower in comparison to the reverse FIA method. Standard addition and near infrared spectroscopy confirmed the validity of the developed method.

Glycol-based fluids are commonly used for deicing/anti-icing of aircraft. It is estimated that approximately 16% of the heated fluid will adhere to the aircraft while about 49% will spill onto the apron and 35% will be carried away by the wind.[1] Deicing/anti-icing fluids contain at least 50% glycol, *i.e.* ethylene glycol or propylene glycol. The International Standards Organisation (ISO) has been actively associated with deicing/anti-icing since 1985 (ISO T20/SC9).

Concern has been expressed for the environmental impact of glycol-based fluids. Contamination of surface drainage with such fluids is known to cause severe pollution problems in receiving waters. Consequently, there is a need for a simple and fast method to determine the glycol content in water effluents from airports. This paper describes a Flow Injection Analysis (FIA) approach combined with refractive index detection (Schlieren optics) to be used for this purpose.

If a sample containing glycol is injected into a carrier stream of pure water a refractive index gradient is formed across the sample zone. When the glycol sample zone passes through a photometric flow-through detector the light will first be focused into the centre of the detection cell and then dispersed from the centre. The detector will thus register an absorbance decrease followed by an increase, *i.e.* a double peak appears. The distance between the two peaks depends, among others, on the sample volume injected.

The first FIA application based on this refractive index phenomenon was published by Betteridge and Ruzicka.[2] They determined glycerol in glycerol/water mixtures by injecting a 50 μl sample into a carrier comprising a 0.001% Bromothymol Blue solution. They used a single line manifold consisting of a 1.4 m long conduit with an inner diameter of 1.0 mm. The conduit was connected to a spectrophotometric flow cell and the detection wavelength was 620 nm. The carrier flow rate was 4 ml/min.

Pawliszyn[3] has reviewed the potential of concentration gradient detection based on Schlieren optics. Sample introduction and detector configuration are crucial since the sensitivity of the detection depends on the change in analyte concentration that can be produced in the detection region. Sucrose could be determined in the concentration range 5×10^{-6}–$10^{-1}M$ using a simple FIA system.[4] Schlieren optics has also been used as a detection principle in capillary separation techniques.[5] An important conclusion drawn by Pawliszyn[3–5] is that the signal obtained in a system based on Schlieren optics is dependent on both the magnitude of the concentration change as well as the distance over which the change occurs.

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This paper describes a simple system for glycol determination based on Schlieren optics using a single line manifold and a spectrophotometric detector.

EXPERIMENTAL

The two basic flow injection system configurations used in this study are depicted in Fig. 1 Figure 1(a) is a common FIA manifold (cFIA) while Fig. 1(b) shows a reverse FIA manifold (rFIA). Figure 1(c) shows a typical detector recording and the principles of three evaluation modes employed. NEG being the negative deflection relative to baseline level, POS the corresponding positive deflection, and TWIN the overall deflection range which is independent of the baseline level. The system was composed of a FIAstar 5010 or 5020 Analyzer combined with a FIAstar 5023 Spectrophotometer with variable wavelength (Tecator, Höganäs, Sweden) The flow cell volume was 18 μl and the studied wavelength range was 400–700 nm. The flow cell entrance channel is J-shaped to prevent trapping of air bubbles while the exit channel is straight. In this application the flow cell was connected "backwards" to the FIA manifold to avoid excessive sample dispersion caused by the J-shaped channel geometry A restriction coil (1 m, 0.35 mm i.d.) was connected to the flow cell outlet to suppress air bubble formation. Thermostatting of conduits was accomplished with a 5101 Thermostat (Tecator, Höganäs, Sweden).

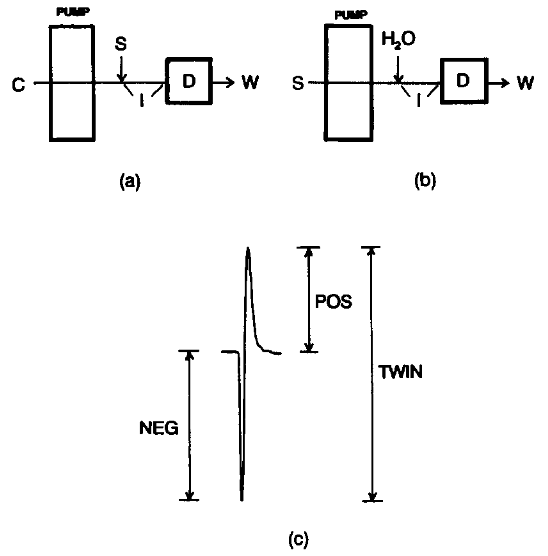

Fig 1 FIA system configurations used for glycol determination (a) common FIA (cFIA), (b) reverse FIA (rFIA), (c) typical output signal where NEG denotes the negative deflection, POS the positive deflection and TWIN the total deflection C = carrier, S = sample, W = waste, l = connection conduit

Reagent grade chemicals were used for preparation of all standard solutions. Glycol samples were obtained from Arlanda airport, Stockholm, Sweden. They were filtered through a 0.45 μm pore size filter before introduction into the FIA system.

A colourless glycol standard solution (3%) was used to investigate the peak height variation as a function of the detection wavelength. The total deflection of the signal output was found to decrease gradually when the wavelength was increased in the range 400–700 nm The maximum decrease amounted to about 14%. This observation relates to "clean" glycol samples only. Some commercial deicing/anti-icing liquids are coloured by a dye called "paraorange" by the manufacturer (Hoechst, Frankfurt am Main, Germany) This dye absorbs light in the wavelength range 450–550 nm. For such coloured samples a much larger decrease will be observed if the detection is made within the absorbing wavelength range For example, the total signal output will decrease as much as 30% for samples containing paraorange if the detection is made at absorbance maximum, *i.e.* at 500 nm.

Standard addition experiments were performed by spiking the samples with pure, concentrated glycol. A near infrared 6500 Analyzer (NIRSystems, Silver Spring, MD, USA) with a 2 mm cuvette was employed for reference measurements. Calibration of the near infrared (NIR) method was made by making a set of aqueous glycol solutions with no dye or corrosion inhibitors added.

RESULTS AND DISCUSSION

Investigation of basic system attributes

Figure 2 shows calibration curves obtained in the concentration range 1–5% of diethylene glycol for various injection volumes, 40–450 μl, using the two system configurations depicted in Fig. 1. The carrier flow rate was 2.1 ml/min (cFIA) and the same flow rate was used for the samples in the rFIA configuration setup. The detection wavelength was 410 nm. It is interesting to note that the negative peak attains a "saturation level" for sample volumes larger than 100 μl using the cFIA approach. This is in accordance with the pattern observed for the front end of a peak in a common FIA system

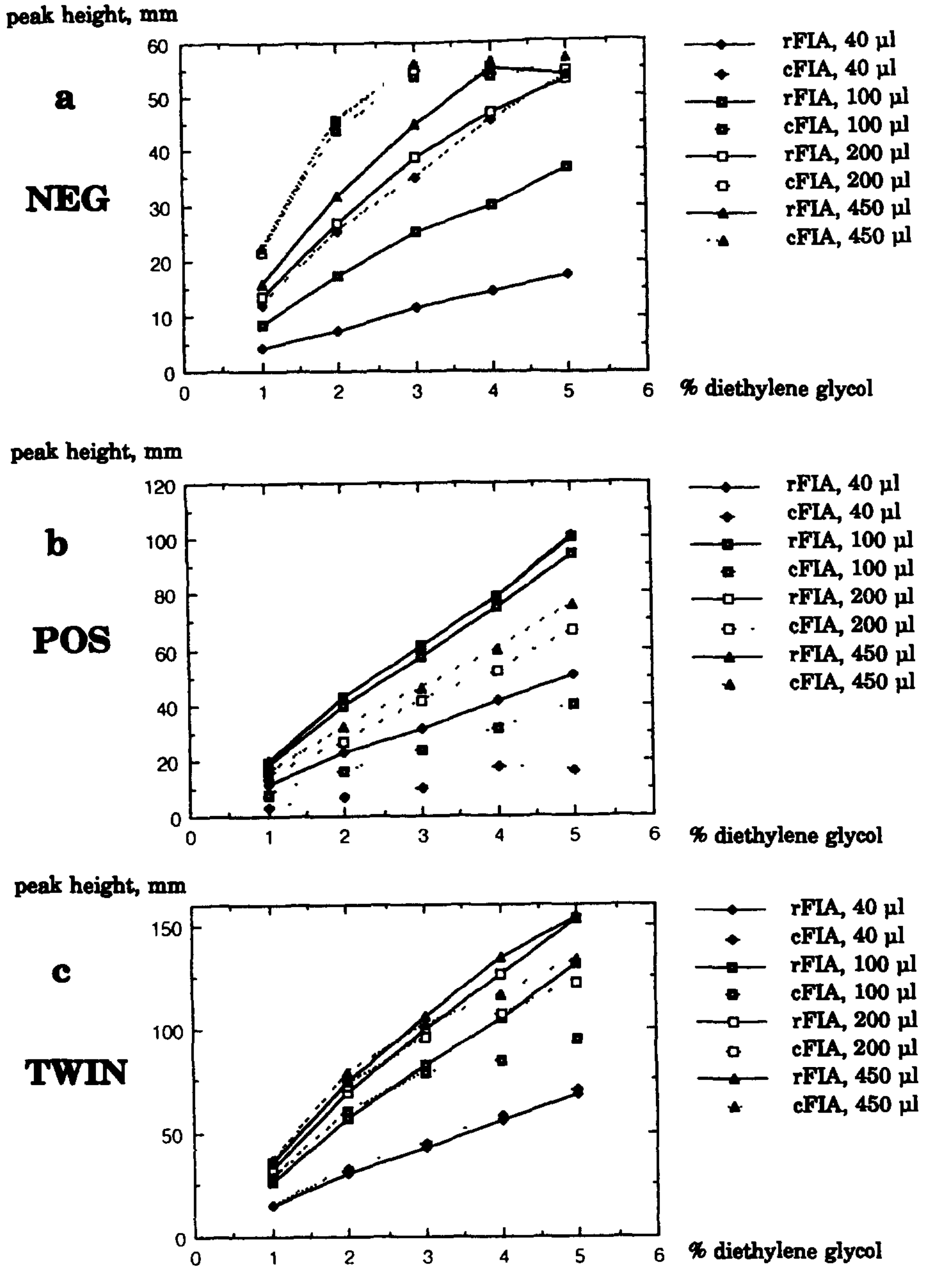

Fig 2 Calibration curves for diethylene glycol (a) evaluation using the negative peak, (b) evaluation using the positive peak, (c) evaluation using the total peak.

when the injected volumes are increased above 100–200 µl.

The twin peak evaluation method, see Fig. 1(c), seems to be a logical and appropriate method of choice. It also appears that the rFIA approach has superior linear behaviour in comparison with cFIA over the concentration range studied.

When using the cFIA approach, flow rate and sample volume have a large influence on the magnitude of the detector response and further on the response time and the sampling frequency. Figure 3 shows the signal response (twin peak evaluation method) as a function of both flow rate and sample volume; Fig. 3(a) obtained for a sample comprising a 2% propylene glycol solution and Fig. 3(b) for a 10% propylene glycol solution. Appropriate response conditions resulted when the flow rate was 0.7 ml/min and the sample volume was 100 µl. The conduit named "l" connecting the injector and the detector in the single line manifold, see

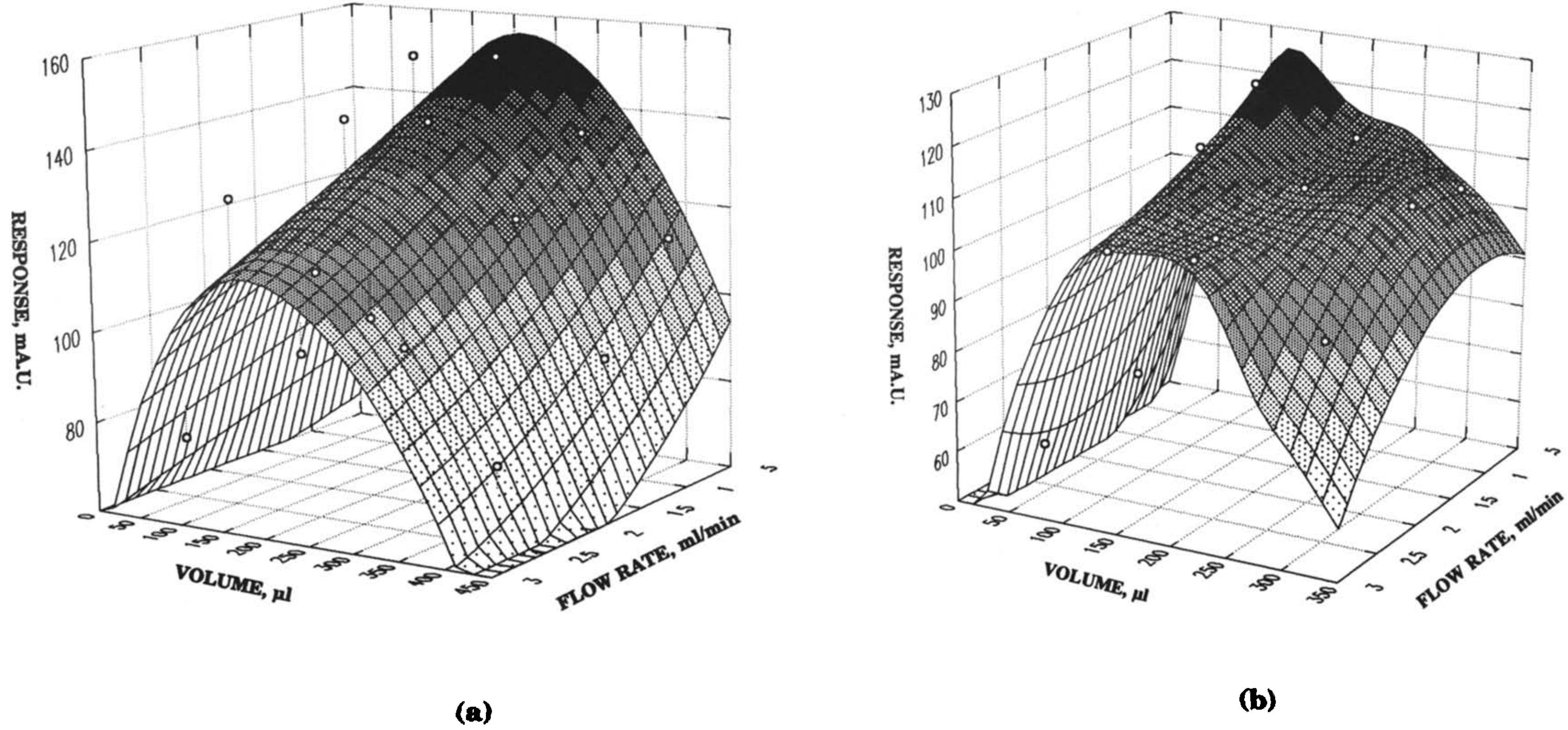

Fig 3 Response curves obtained in cFIA mode for varying flow rate and sample volume (a) sample comprises 2% propylene glycol, (b) sample comprises 10% propylene glycol

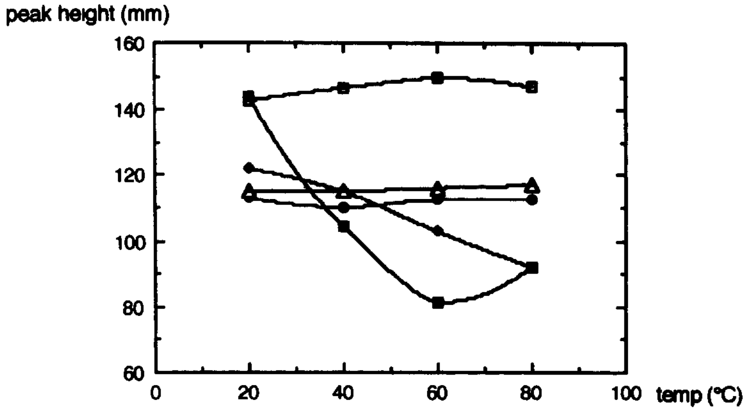

Fig 4 Effect of keeping individual parts of the FIA system at different temperatures while keeping the remaining parts at 22°C ☐ water before introduction into the injector (rFIA), ◆ glycol sample before introduction into the injector (cFIA), ● glycol sample before introduction into the pump (rFIA), △ water carrier before introduction into the pump (cFIA), ■ liquid just prior to inlet into the flow cell of the detector (both rFIA and cFIA)

Fig. 1, had an inner diameter of 0.5 mm and a length of 10 cm in the preferred setup. The conduit length can be increased to at least 40 cm; whereby the signal response was found to decrease only slightly. The response time of the system was, of course, correspondingly increased for the longer conduit length. A conduit with an inner diameter of 0.7 mm was also tested and, as expected, the signal response decreased drastically. It appears that there is a straightforward relationship between the magnitude of the signal and the dispersion coefficient of the FIA system for this type of detection principle. the lower the dispersion coefficient the larger the signal.

When the rFIA setup was used, similar observations as for the cFIA setup were made regarding the relationship between the injected volume and the magnitude of the detector response. However, the feeding of samples was more of a problem in the rFIA case since air usually was used to separate the different samples and this results in a reduced sampling frequency.

Figure 4 shows the detector response obtained when individual parts of the system were kept at elevated temperatures while the remaining parts of the system were kept at room temperature, *i.e.* at 22°C. The vital part of the system with respect to temperature is evidently the connection conduit "l". The efficient heat transfer in the narrow bore conduits in the system levels out temperature differences between the bulk of the liquids at the introduction into the system and the conduit system. The response decrease observed at elevated temperatures is most likely due to enhanced mixing in the interface region between the sample and the carrier, thereby decreasing the concentration gradient.

Dynamic range

The targeted dynamic range for the described method is 0–5% glycol in aqueous solutions. A glycol concentration of 0.05% can readily be detected. It is possible to determine even lower concentrations of glycol if precautionary measures like filtering and degassing of samples are taken. For glycol concentrations above 5% the calibration curve becomes nonlinear for both the cFIA and the rFIA approaches. For cFIA, the carrier stream can then be modified by adding glycol. For rFIA, glycol can be added to the injected water, *i e.* in either approach the overall change in refractive index is adapted to the linear region of the detector used Addition of an inert salt or a third solvent to the carrier had a similar effect but this approach has not been investigated further.

Real samples

Samples were collected at Arlanda airport during the period November–December 1992. The samples were of two types· "glycol A" which refers to samples with a relatively high content of glycol collected by a special "vacuum cleaner" in operation at the apron immediately after deicing of an aircraft, and "glycol B" which is the diluted, residual glycol solutions led to and kept in large, open reservoirs situated in the vicinity of the airport. Glycol A solutions can be distilled so that the glycol is recycled while glycol B solutions are biologically treated

Table 1 Determination of glycol in samples containing paraorange using reverse FIA (rFIA) and near infrared spectroscopy (NIR)

rFIA	NIR
10 0	10 3
9 2	10 0
8 2	9 5
8 0	10 6

to reduce the content of oxygen consuming organic material.

Since the main objective with this work was to develop a fast and simple method for the environmentally important glycol B solutions, a large number of these solutions were collected. The solutions originated from different sites at the airport. They were all found to have a glycol content in the range 0 25–0 45%. Based on the results shown in Fig. 3 a carrier flow rate of 0.7 ml/min was selected. The injection volume was 100 μl both for the cFIA and the rFIA running modes. The conduit length connecting the injector and the detector was 10 cm. Pure propylene glycol solutions were used for calibration purposes and the rFIA principle was preferably applied. Standard addition experiments as well as an alternative assay method using near infrared spectroscopy confirmed completely the validity of the developed rFIA method. The differences in results obtained with the rFIA method and results obtained with near infrared spectroscopy were always less than 0.02% in absolute terms. This finding is expected since the sample matrix containing species that might interfere is so diluted.

A limited number of glycol A samples were also collected and the glycol content was determined both in diluted and undiluted solutions using rFIA and NIR Glycol A samples diluted down to 0.2–2.0% behaved exactly like glycol B solutions, *i e* the absolute deviations between values obtained with the two methods were always less than 0.02%. At higher concentrations, however, slightly larger values were obtained with the rFIA method in comparison to the NIR method. At concentrations above 5% the bias was obvious. Table 1 shows results obtained for undiluted glycol A solutions. The glycol A samples are coloured with paraorange as mentioned earlier while the calibration of the NIR method was performed with pure, uncoloured standards. This might explain the consistently larger values obtained with the NIR method in comparison with the FIA method. Unfortunately, there were too few samples and standards available to build a more reliable calibration procedure based on partial least squares (PLS) for the NIR application. Nevertheless, it can be concluded that the developed FIA method should be applied with care for glycol concentrations exceeding 5%. The use of coloured standard solutions in the high concentration range or adding glycol to the water solution injected in the rFIA method might overcome this bias.

CONCLUSIONS

An analytical system comprising a simple, single-line flow injection manifold can be used in combination with detection based upon Schlieren optics to determine glycol in deicing/anti-icing liquids in the concentration range 0–5%. The rFIA principle is to be preferred to common FIA, *i.e.* pure water is injected into a carrier of sample. The detection limit is 0.05% glycol in aqueous samples.

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