

Determination of Ethanol Using Flow Injection Enthalpimetry

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A flow injection enthalpimetric method for the determination of ethanol in fuel-grade ethanol, based on the heat of dilution of ethanol, is described. The accuracy and precision were 0.05% of ethanol; interferences by several substances are discussed. A similar procedure was also applied to the determination of ethanol in wines and spirits after distillation, yielding a precision of 0.03–0.1% of ethanol. The sampling rate in both procedures is 110 h⁻¹.

Keywords: Ethanol determination; enthalpimetry; flow injection analysis; fuel-grade ethanol

The extensive use of ethanol as a fuel and in fuel mixtures has increased the need for simple, fast and precise analytical methods for quality control purposes. Also, the determination of ethanol is important in the wines and spirits industry. Ethanol is usually determined by measuring the specific gravity, after distilling the sample. The increasing demand for rapid analytical results has prompted the development of an automatic method.^{1,2}

Enthalpimetric measurements have been proposed^{3,4} for the determination of ethanol in wines and spirits. The heat of dilution of ethanol samples can be correlated with the concentration of ethanol,⁵ and the purpose of this work was to study the possibility of using this property in the development of a rapid procedure based on flow injection analysis.

Experimental and Results

Analytical-reagent grade chemicals were used throughout.

Apparatus

The experiments were performed using a flow enthalpimeter as described previously.⁶ It consists of a peristaltic pump, which impels the fluids towards an insulated 8-l water-bath, in which the injector and flow manifold are placed. Temperature differences are measured with a pair of twin thermistors connected to a d.c. Wheatstone bridge, the output voltage of which is monitored with a strip-chart recorder.

Manifold

The manifold used is shown in Fig. 1. Technicon Solvaflex tubing of 0.5 mm i.d. was used for all streams. Pulse dampers (D₁ and D₂) similar to those previously described⁷ were used. Temperature equilibration coils (E₁–E₄) were made of 1 m long stainless-steel tubes of 0.5 mm i.d. A laboratory-made proportional injector⁸ (I) was used. The indicator (T_i) and reference (T_r) flow cells were modelled as T-connectors, with the thermistors mounted perpendicular to the fluid streams. The injector and the flow cells should be made of nylon to avoid attack by concentrated ethanol. The flow cells have a volume of about 17 µl. The reactor (R) was made of Solvaflex tubing of 2.5 mm i.d. and 3.5 mm o.d., packed with glass beads (35–46 mesh).

Determination of Ethanol in Fuel-grade Ethanol

For the analysis of fuel-grade ethanol (range of ethanol concentration 85–100%), both the carrier and diluent were anhydrous ethanol. Fuel samples of 100 µl were introduced directly into the flow manifold and the resulting enthalpimetric peaks were compared with those of standard solutions.

Calibration solutions were standardised by means of pycnometry using 10-ml pycnometers according to well accepted procedures.⁹

Typical enthalpimetric signals are shown in Fig. 2. The calibration graph is linear for concentrations higher than 90%. At these concentrations the magnitude of the enthalpimetric signal (ΔT , 10⁻³ °C) can be correlated with the concentration of ethanol (C_{EtOH} , % m/m) by the equation $\Delta T = 2203.5 - 23.514 C_{\text{EtOH}}$, with a correlation coefficient of 0.9998. As the specifications for fuel-grade ethanol¹⁰ require that the concentration of ethanol must be between 91.1 and 93.9%, the linear part of the calibration graph is appropriate for the analysis of fuel-grade ethanol. For concentrations lower than 90% the calibration graph is curved; it passes through a maximum at about 85% and then the sign of the slope changes. The enthalpimetric signals for the lower concentration region show a different profile, with double peaks.

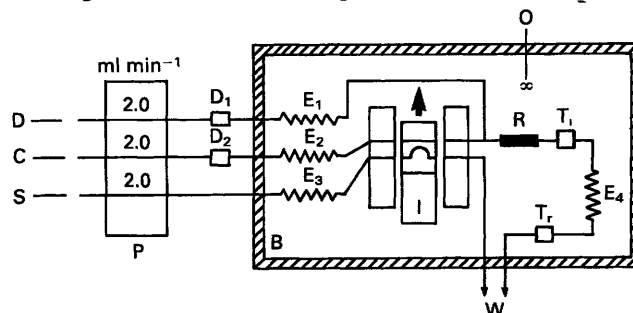


Fig. 1. Flow manifold for the determination of ethanol. (D) Diluent; (C) carrier; (S) sample; (P) peristaltic pump; (D₁) and (D₂) pulse dampers; (E₁)–(E₄) equilibration coils; (B) insulated water-bath; (I) injector; (R) reactor tube; (T_i) and (T_r) indicator and reference thermistor cells; (O) overhead stirrer; and (W) waste

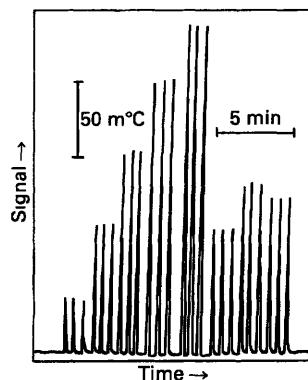
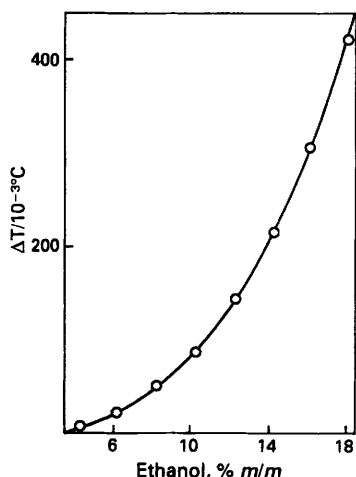


Fig. 2. Typical enthalpimetric signals for the determination of ethanol in fuel-grade ethanol. From left to right are shown calibration runs, with standard solutions of ethanol concentration 96.07, 93.82, 91.80, 89.76 and 87.66%, followed by the signals of three samples. All measurements performed in triplicate

Table 1. Comparison of results of the analysis of samples of fuel-grade ethanol

Sample	Ethanol concentration, % m/m		Absolute difference, % m/m
	Pycnometric method	Enthalpimetric method	
SH ₁	93.94	93.89	-0.05
SH ₂	93.31	93.23	-0.08
SH ₃	93.96	94.00	+0.04
SF ₁	92.57	92.49	-0.08
SF ₂	92.86	92.84	-0.02
SF ₃	92.08	92.13	+0.05

**Fig. 3.** Calibration graph for the determination of ethanol in wines and spirits

Therefore, confusion with the signals (of the same height) of samples of higher concentration is avoided.

The effect of interferents on the enthalpimetric signal was studied by adding to a synthetic sample substances that may be present in fuel-grade ethanol. The compounds tested were benzene, acetic acid, acetaldehyde, amyl alcohol and ethyl acetate. No interference from these substances was observed for the concentrations that are usually found in fuel-grade ethanol.

The accuracy of the proposed method was evaluated by analysing real samples of fuel-grade ethanol and comparing the enthalpimetric values with those obtained by pycnometry. The results are shown in Table 1 and indicate that the average absolute difference is 0.05% of ethanol. The same value was found for the precision of the method, obtained by repeating ten times the analysis of three different samples of fuel-grade ethanol.

Determination of Ethanol in Wines and Spirits

The enthalpimetric procedure was also applied to samples containing lower concentrations of ethanol. In this instance, water was used as the diluent because it was observed that

more precise results are obtained when the sample and the diluent have similar densities. For the determination of ethanol in wines and spirits the samples should first be distilled and then water added in order for the final ethanol concentration to fall within the most precise range for measurements (around 12%); 100 µl are introduced into the flow manifold, using water as both carrier and diluent. Typical calibration data obtained with standard solutions are shown in Fig. 3. The precision in the ethanol concentration range 6–12% was found to vary from 0.03 to 0.1%, being better for samples with higher concentrations of ethanol.

The interference on the enthalpimetric signal caused by substances normally found in wines, such as glucose, fructose, tartaric acid and malic acid, was investigated. At the levels of concentration at which they are usually found in these samples, these substances were found to affect the magnitude of the signal. For this reason the enthalpimetric measurement should be performed after distillation of the sample, as is recommended in the official method for the determination of ethanol in wines.¹¹ In the wine distillate the interferents are not present in sufficient amounts to affect the enthalpimetric measurements significantly.

Comparison with Other Methods

The precision and accuracy of the enthalpimetric method are comparable to those of other reported procedures^{2–4} for the determination of ethanol in fuel-grade ethanol, and are slightly lower for the determination in wines and spirits. The enthalpimetric method is faster, allowing a sampling rate of 110 h⁻¹. Also, the instrumentation used in flow injection enthalpimetry is simple and inexpensive and consumption of the reagents and sample is very low.

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