IC APPLICATION NOTE AN

Chloride and sulfate in ethanol used as biofuel

Determination of sulfate and inorganic chloride in fuel ethanol by direct injection suppressed ion chromatography

In times of skyrocketing gasoline prices, ethanol fuel mainly derived from the fermentation of sugar cane (in Brazil) and corn (in the USA and Canada) – is a promising renewable high-octane vehicular fuel. A major drawback, however, is the contamination with inorganic salt ions such as chloride, nitrate and sulfate. These ions can affect the engine performance because of precipitating salts clog filters and fuel injector nozzles. Furthermore, these ions enhance corrosion in the vehicle components in contact with the fuel. Hence there is an urgent need for standards defining quality specifications and test methods. While the analysis of sulfate is specified in a few ASTM norms, until recently, the ASTM D 4806-06 standard – the specification for denatured fuel ethanol – provided no guidelines for total and potential sulfate. Recognizing the need for validated methods for quality control, ASTM balloted and approved a sulfate specification for fuel ethanol stipulating a maximum level of sulfate in ethanol of

4 parts per million (ppm). The corresponding inorganic chloride contamination limit in ethanol is proposed at 40 ppm. In this note a convenient direct injection suppressed ion chromatographic method

SAMPLE

Ethanol

EXPERIMENTAL

The sample is injected directly and analyzed using method parameters given in Table 1.

Quantification of the anions was achieved by integration of the resulting peaks compared with an external calibration curve.

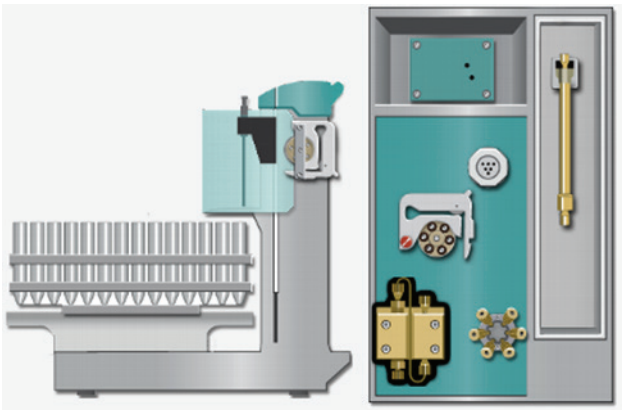

Figure 1. Instrumental setup including a 930 Professional IC Vario ONE/SeS/PP and 919 Professional Sample Processor (R).

RESULT

This application note demonstrates direct injection IC method to determine whether ethanol used as a blending agent in gasoline meets the chloride and sulfate specifications as per ASTM D 4806.6.

TABLE 1. IC method parameters

Column	Metrosep A Supp 5 – 250/4.0
Eluent	5.0 mmol/L sodium carbonate
	1.0 mmol/L sodium hydrogen carbonate
Flow rate	0.6 mL/min
Injection volume	20 uL
Detection	Suppressed conductivity

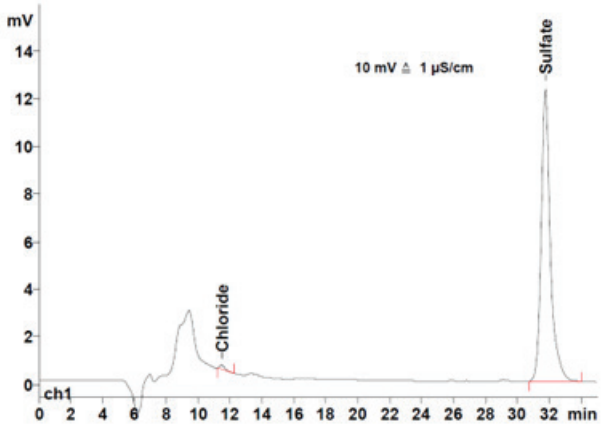

Figure 2. Chromatogram for sulfate and chloride in ethanol.

CONCLUSION

The determination of total and potential sulfate and inorganic chloride in fuel ethanol is the subject of ASTM D 7319. External calibration curves of peak area versus concentration are linear in the range 0.625…50 ppm for chloride and 0.25…20 ppm for sulfate. Corresponding correlation coefficients are higher than 0.9998 and the limits of detection for chloride and sulfate are 0.6 and 0.2 ppm, respectively. Even after 1500 ethanol injections containing denaturants and hydrogen peroxide, the analytical unit still provides stable retention times, repeatable peak areas and consistent concentration values. The excellent repeatability and reproducibility of the applied trichamber «MSM II» suppressor demonstrates its ruggedness in long-term use. For all samples investigated, standards and blanks, conductivity detection provide accurate and precise results. The presented direct injection IC system is solvent compatible and ensures the accurate and precise determination of sulfate and other anions in ethanol samples in full compliance with ASTM D 4806-06c.

REFERENCES

1. (1) D.W. Rowe, Meeting the analytical requirements for sulfate in Ethanol. In Ethanol Producer Magazine 152-154 (October 2006).

2. (2) Metrohm Application Work AW-US6-0110-072005, Determination of sulfate in denatured ethyl alcohol by direct injection ion chromatography and suppressed conductivity.

3. (3) J. Gandhi, R. Benton and D.W. Rowe, Determination of bromide and sulfate in flame retardants by ion chromatography, LC/GC The Application Notebook (February 2005).

4. (4) ASTM D 4806 – 06c Standard specification for denaturated fuel ethanol for blending with gasoline for use as automotive spark-ignition engine fuel.

5. (5) ASTM D 7319 – 07 Standard test method for determination of total and potential sulfate and inorganic chloride in fuel ethanol by direct injection suppressed ion chromatography.

wo orders of magnitude lower, showing the suitability of the present single quadrupole ICMS method for drinking water quality measurements.

Analytes:	**Sulfate & Chloride**
Matrix:	**Ethanol**
Method:	**Ion Chromatography**
Industry:	**Petroleum**
Standards:	**ASTM**

IC Application Note AN-S-4xx, Version 1 – 2022-04
AW IC IN6-2210e-052022