Determination of sulfate and chloride in denatured ethyl alcohol according to ASTM D 7319

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Metrohm Ion analysis

Ion Chromatography

Abstract

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 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 number of ASTM norms, until recently, the ASTM D 4806-06b 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 paper a convenient direct injection suppressed ion chromatographic method for determining chloride and sulfate in denatured ethanol samples is presented. The described method is the subject of the recent ASTM D 7319 and the results obtained fully comply with ASTM D 4806-06c.

System setup

- 861 Compact IC with «MCS» («MCS» not shown)
- «MSM II» Metrohm Suppressor Module (trichamber)
- 838 Advanced Sample Processor
- Metrosep A Supp 5 – 150
- Metrosep RP Guard
- M-Pak® for A Supp 5

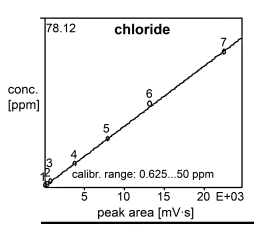
Experimental conditions

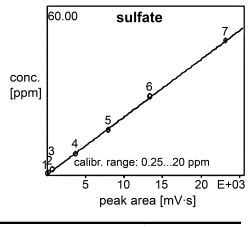
The determination of inorganic sulfate and chloride in ethanol samples involves the direct injection of 20 µL ethanol into the ion chromatograph. For determining the potential sulfate, 0.5 mL of 30% hydrogen peroxide solution is added to 9.5 mL of the ethanol sample.

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

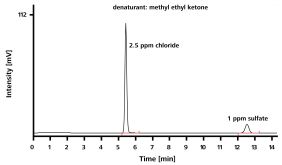
Eluent:	3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$
Column:	Metrosep A Supp 5 – 150
Column temperature:	35 °C
Flow rate:	0.7 mL/min
Sample size:	20 µL
Detector:	Conductivity after sequential suppression
Suppressor solutions:	100 mmol/L H_2SO_4 at 0.5 mL/min (regenerant)
	High purity water at 0.5 mL/min

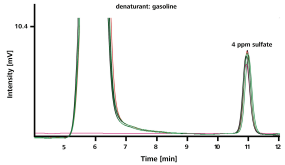
Calibration (conductivity detector)





	Calibration solution							Correlation coefficient
	1	2	3	4	5	6	7	
Chloride [ppm]	0.625	1.25	2.5	6.25	12.5	25	50	0.99982
Sulfate [ppm]	0.250	0.50	1.0	2.50	5.0	10	20	0.99989





Suppressor and column ruggedness

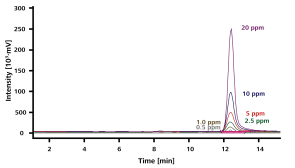
Injection number	Sample ID	Concentration [mg/kg]	Peak area [mV · s]	Retention time [min]
1	denat. EtOH + H_2O_2 + SO_4^{2-}	5.683	123.635	12.54
2	denat. EtOH + H_2O_2 + SO_4^{2-}	5.885	124.023	12.53
⋮	⋮	⋮	⋮	⋮
1505	denat. EtOH + H_2O_2 + SO_4^{2-}	5.761	123.091	12.54
	Average	5.611	123.634	12.540
	Std. Dev.	0.131	0.574	0.027
	RSD [%]	2.333	0.465	0.213

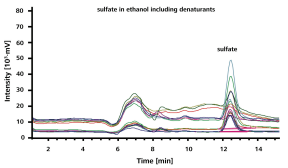
Even after more than 1500 injections neither the denaturants nor the hydrogen peroxide or the ethanol itself affect the operational integrity of the IC system.

		Repeatability (% RSD)		Reproducibility (% RSD)	
	[ppm]	«MSM II» (trichamber)	Continuous	«MSM II» (trichamber)	Continuous
Total chloride	1	0.07	0.07	0.42	0.42
	20	0.56	0.56	3.40	3.40
	50	1.06	1.06	6.45	6.45
Total sulfate	1	0.09	0.25	1.22	1.60
	4	0.2	0.61	2.86	3.99
	20	0.55	1.77	7.73	11.54
Potential sulfate	1	0.13	0.27	0.97	1.43
	4	0.33	0.71	2.55	3.73
	20	1.01	2.16	7.80	11.32

The rugged «MSM II» suppressor is ideally suited for the direct injection of organic solvents.

Tandem IC-Conductivity-MS





	Sulfate concentrations [ppm]		
	MS detector		Conductivity
Sample ID	m/z 97	m/z 99	detector
Blank Ethanol	0.017	0.015	0
CCC - 1.2 ppm	1.190	1.279	1.13
CCC - 2.4 ppm	2.354	2.361	2.46
Blank Ethanol	0	0	0
Sample 1	0.019	0.020	0
Sample 2	0.02	0.019	0.02
Sample 3	0	0	0
Sample 4	2.061	2.111	1.88
Sample 5	4.483	4.382	4.43
Sample 6	5.275	5.217	5.73
Sample 7	19.441	19.189	19.89
Sample 8	1.003	0.945	0.88
Sample 9	1.012	1.042	1.02
Sample 10	1.136	1.283	1.11
Check Std (10 ppm)	10.648	10.569	10.55
Check Std (25 ppm)	25.748	26.298	25.30
Blank DI	0.017	0.015	0

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 investigated samples, standards and blanks, both mass spectrometric and 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.

Literature

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

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

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

(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.

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