Determination of Silicate in Waste and Recycled Engine Coolants using Capillary Electrophoresis

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Objective

Develop a robust capillary electrophoresis method for the detection of silicate in waste and recycled engine coolants.

Introduction

Waste Coolant Recycling

- Glycol-based coolants are ubiquitous in automotive engines and industrial machinery¹
- Recent European Union legislature has driven an increase in the recycling of waste coolants²

Silicate in Engine Coolants

- Silicate is considered the most effective corrosion inhibitor for metal surfaces in engines¹
- Complex equilibria between solid colloids and soluble monomers impose need for organosilicate stabilizers¹
- Capillary electrophoresis (CE) has proven to be an effective technique for silicate and coolant additive analyses³

Figure 1. Equilibria between soluble silicate and insoluble polymer colloids.

Methods

Effects of Background Electrolyte

Figure 2. Electropherograms of 10 mg L⁻¹ silicate standard with 20 mg L⁻¹ methionine using A) 2,6-pyridinedicarboxylic acid, B) sodium benzenesulfonate, C) tyrosine, and D) Na₂CrO₄ background electrolyte. Electrolyte composition: 10 mM A/B/C/D, 3 mM TTAB, 2 mM Na₂CO₃, adjusted to pH 11.0 ± 0.1 with NaOH.

Method Validation

Figure 3. (Left) Silicate calibration curve using Na₂CrO₄ background electrolyte. Silicate peak areas were normalized to IS and mean values are reported.

Table 1. (Right) Analytical figures of merit using Na₂CrO₄ background electrolyte, †n = 18.

Parameter	Value
Intercept (±SE)	0.008 (±0.006)
Slope (±SE)	0.1019 (±0.0003)
LOD (mg L ⁻¹)	~0.29
LOQ (mg L ⁻¹)	~0.95
Linearity (R ²)	0.99997
Migration Time	
Reproducibility (%RSD) [†]	1.23
Mean Relative Peak Area	
Reproducibility (%RSD) [†]	2.34

Preliminary Coolant Results

Figure 4. Recycled automotive coolant diluted 9:1 and pH adjusted to 11.0 ± 0.1 without spike (left) and with 10 mg L⁻¹ silicate added (right). Spike recovery was calculated to be 103.4%.

Conclusions

- Sodium chromate background electrolyte shows highest potential for use in coolant recycling industry
 - Viability is limited by significant matrix effects imposed by some coolant samples
- Sodium benzenesulfonate background electrolyte provided desirable performance, but is incompatible with most coolants
- If decomposition is mitigated, tyrosine may prove to be superior background electrolyte
 - Higher sensitivity and shorter migration time observed with tyrosine background electrolyte

Future Directions

- Attempt preconcentration or purification techniques (e.g. SPE) to minimize matrix effects in coolant samples
- Investigate effects of organosilicate stabilizer on coolant analysis
 - High pH and/or temperature treatment to release bound silicate
 - Analysis of industrial inhibitor mixture
- If method proves unsuccessful, contactless conductivity detection may also be explored

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