

## Fast and comprehensive analysis of inorganic and organic anions in car engine coolants by CE-UV

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The analysis of small inorganic and organic anions in engine coolants is mostly carried out with ion chromatography. However, this method is not suited with the recent growing complexity of engine coolants and composition due to matrix effect and thus cannot adequately address the steadily increasing performance requirements of car engines. Since quality control of coolants both as product but also under stress conditions when in use requires the analysis of inorganic and organic ions in a matrix of mostly uncharged matrix components (e.g. up to 50 % ethylene glycol), capillary electrophoresis (CE) appeared to be a promising alternative to IC. Therefore, in this study, a new CE method with indirect UV-detection is proposed.

Specifications require the analysis of the inorganic anions chloride, nitrate, sulfate, nitrite, fluoride and phosphate and the organic anions oxalate, formate, succinate, acetate and glycolate, most of them impurities due to the decomposition of ethylene glycol. These analytes exhibit a broad range of the absolute electrophoretic mobilities (from  $-42.4$  to  $-79.1 \times 10^{-9} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ ) [1] and corresponding  $\text{pK}_a$  values (from  $-7$  to  $+12.32$ ) [2], which challenges CE method development. Method optimization included a tedious pH optimization to enable a quantitative analysis of all analytes in one run. Especially, the separation of the both analyte pairs of nitrite/nitrate as well as glycolate/acetate was challenging and reached using pyromellitic acid as probe ion at pH 3. Hexamethylene diamine was added to the BGE and served as counterion and EOF modifier simultaneously, which helped to avoid the evolution of system peaks. The analysis was carried out on a bare-fused silica capillary at a voltage of  $-30$  kV. For the first time, all analytes specified as well as two internal standards (potassium dichromate and  $\alpha$ -hydroxyisobutyric acid) could be separated. Analysis time was short with only 8 min plus 2 min rinsing steps.

The method was validated with respect to specificity, linear range (4.6-19.8 mg/L), limits of detection (0.8-15.1 mg/L) robustness (method transfer to different instrumentation), precision (6.7 % RSD on average for peak area) and matrix effects. Analysing engine coolants resulted in system peaks due to more complex compositions of the sample zone. Nevertheless, quantification of 8 (out of 11) anions was possible via external calibration and/or standard addition. Sample preparation only included dilution with water.

Especially the short analysis time in combination with high separation efficiency makes CE with indirect UV detection attractive compared to common IC methods.

[1] T. Hirokawa, M. Nishino, N. Aoki, Y. Kiso, Y. Sawamoto, T. Yagi, J.-I. Akiyama, *J. Chromatogr. A* **1983**, 271, D1–D106.

[2] E. Riedel, C. Janiak, *Anorganische Chemie*, De Gruyter, Berlin, Boston, **2011**.