Short Communication

Indirect CE-UV detection for the characterization of organic and inorganic ions of a broad mobility and pK_a range in engine coolants

An alternative CE-(indirect ultraviolet) method for the analysis of inorganic and organic anions in ethylene glycol-based engine coolants is presented using a BGE with 4 mM pyromellitic acid and 3.4 mM 1,6-hexamethylene diamine, pH 3. Baseline separation of six inorganic (e.g. nitrite, nitrate, and sulfate) and five organic anions (e.g. acetic and glycolic acid) was achieved. Quantification of 8 out of 11 specified anions was possible in stressed engine coolant samples after simple aqueous dilution. LODs between 0.8 and 15.1 mg/L with RSD values of peak areas between 2.6 and 11.9% were obtained. Some limitations due to matrix effects can be overcome with slight adaptations of the BGE. The flexibility of the method is vital regarding the increasing demands for the composition of engine coolants for pollution reduction.

Keywords:
Ethylene glycol matrix / Nitrite/nitrate separation DOI 10.1002/elps.201900198
concentration of hydronium ions at the advantageous pH

nitrite-

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see Figure 1C) allowed to separate nitric acid from nitrous

α

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Figure1B). For the separation of nitrate and nitrite complex-

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requires control and fine-tuning of the direction and mag-
nitude of the EOF, which can be accomplished with differ-
ent coatings [12, 13]. We investigated coatings of high re-
versed EOF (statically adsorbed polybrene [14] and EOTrol
HR [15,16]) and strongly suppressed EOF (static PVA [17,18]
and statically adsorbed EOTrol LN [15,16]). Resolution with
these coatings was insufficient. Using EOF reduction via the
dynamic EOF modifier HMDA [19,20] was promising for fur-
ther method development.

Advantageously, HMDA could be used for both EOF con-
trol and buffering serving as counterion. This strategy re-
duced the number of buffer components to a minimum and
thus also the number of system peaks disturbing quantifica-
tion when using indirect UV or C^4D detection [11,21] (for an
example, see Figure 1A).

The adjustment of the pH for highest selectivity was sup-
ported using simulations with PeakMaster [22]. To-
gether with experiments we saw that pH values >7 resulted
in comigration of acetic and glycolic acid due to very
similar effective electrophoretic mobilities at full charge
(see Table 1). Only at lower pH, differences in their pK_a
values and thus their effective electrophoretic mobilities
were high enough to achieve baseline separation. At pH
<, acetate was insufficiently separated from the sample plug
due to too low dissociation. The separation of sul-
furic acid, nitric acid, and nitrous acid was challenging: comi-
gration of nitrate and nitrite occurred at pH >5 (see
Figure 1B). For the separation of nitrate and nitrite complex-
eation with either cadmium ions [23] or cyclodextrin [24] was
successfully applied in the past. The addition of 40 mmol/L
α-CD (BGE = 20 mM MES, 20 mM l-histidine, EOTrol LN,
see Figure 1C) allowed to separate nitric acid from nitrous
acid; however, only with concurrent comigration of the
nitrite-α-CD-complex and sulfate. Unfortunately, the high
concentration of hydronium ions at the advantageous pH
<4, precluded conductivity detection [25] (see Figure 1D).

Best separation efficiency would be obtained with a probe
ion of an electrophoretic mobility close to the analytes [26,27].
Due to the formation of disturbing system peaks, a combina-
tion of two probe ions (see Doble and Haddad [28]) to account
for the broad mobility range of the analytes of interest (see
Table 1) was not successful. Finally, PMA with an interme-
iate electrophoretic mobility and a suitable lowest pK_{a1}
of 1.9 was chosen [29]. Baseline separation of all analytes was
achieved after fine-tuning of the BGE to pH 3. A compro-
mise had to be found for the separation of the most critical
anions, nitrite, sulfate and nitrate, the sufficient dissociation
of acetic and glycolic acid and the avoidance of disturbing sys-
tem peaks. To the best of our knowledge, this is the first time
that these five anions were included in one CE-(indirect)UV
method.

The final method was: PMA (c = 4 mM) served as probe
ion and HMDA (3.4 mM) as counter ion and EOF suppressor.
Electropherograms were recorded at 220 nm using a separa-
tion voltage of −30 kV. All 11 inorganic and organic analytes
and two additional internal standards, dichromic acid, and
HIBA, were baseline-separated (see Figure 2, Trace A).

Some matrix effects were present: Figure 2, traces B and
C show two different stressed cooling agent samples. Due
to partial comigration of acetate and a matrix compound, it
could only be identified but not quantified. Similarly, quan-
tification of chloride and nitrate was hindered in matrix due
to a system peak present only for stressed samples.

Standard addition was performed in triplicates with addi-
tion of 0.05, 0.10, and 0.15 mM analytes to samples (1:10
diluted with water). External calibration (0.07–0.3 mM) was
performed in the linear range in duplicate. Determination of
method precision was conducted with ten consecutive runs
at analyte concentrations of 0.10 mM in a cooling agent sam-
ple. The electropherograms were illustrated and evaluated
with Origin. Quantification was performed using the tool
“Peak Analyzer” and LODs were determined according to
The use of HMDA as a dynamic EOF modifier is advantageous as it allows to easily adapt the BGE when specific analytes are prioritized; for instance, suitable conditions to analyze phosphate, glycolate, acetate, and succinate were obtained using 20 mM benzoic acid as probe ion and increasing the pH to 4.5. Electropherograms for standard and sample measured under these conditions are shown in Figure 2, Traces D and E.

To our knowledge, this is the first CE-(indirect ultraviolet) method capable to analyze nitrate and nitrite as well as glycolate and acetate in one run, which was possible reducing system peaks having HMDA serving as buffering counterion and EOF modifier. The quantification of most analytes was possible in stressed cooling agents with sufficient LOD. Further optimization is only possible using separate methods for two sets of analytes. Using HMDA in both methods, no special rinsing procedures will be necessary and analysis time can still be kept clearly below 10 min per run, giving rise to analysis times comparable to ion chromatography, though at higher matrix tolerance.
Figure 2. Selected electropherograms for standard and samples. Peak numbering as in Table 1; Peak 12 and 13: internal standards dichromate, HIBA. (A and D) aqueous 0.5 mM standard; (B) 1:10 diluted stressed cooling agent Sample 1; (C) 1:10 diluted stressed cooling agent Sample 2. (E) 1:10 diluted spiked (0.5 mM) stressed cooling agent Sample 3. BGE: (A–C) 4 mM PMA, 3.4 mM HMDA, pH 3; (D, E) 20 mM benzoic acid (BA), 3 mM HMDA, pH 4.5. Injection and internal pressure: (A) 250 mbar·s, 30 mbar; (B and C) 1600 mbar·s, 60 mbar; (D and E) 250 mbar·s, 100 mbar, separation voltage: –30 kV.

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