

TECHNICAL NOTE

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The Use of Capillary Electrophoresis in the Detection of Monomethylamine and Benzoate Ions in the Forensic Examination of Explosives Residues

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ABSTRACT: Capillary electrophoresis (CE) is used in the ATF Forensic Science Laboratories for the analysis of inorganic ions commonly encountered in post-blast residues including monomethylamine (MMA) and benzoate ions. Monomethylamine nitrate is found in Tovex[®], a water gel explosive. Sodium benzoate is added to Pyrodex[®], as a fuel and burn rate modifier. In the analysis of explosive residues, these ions are used as an indicator for the presence of Tovex[®] and Pyrodex[®]. Traditionally, these two ions, along with other ions of interest were analyzed by spot tests and ion chromatograph (IC). CE is currently being used in place of spot tests as a confirmation technique for IC.

KEYWORDS: forensic science, explosives, capillary electrophoresis, monomethylamine, benzoate

The analyses of cations and anions are frequently performed in post-blast explosive cases. The Bureau of Alcohol, Tobacco, and Firearms (ATF) Forensic Science Laboratory utilizes an array of techniques in the detection of these ions. Chemical tests were traditionally used but are being replaced by more sensitive and reproducible instrumental approaches (8,11). Additionally, wet chemical tests do not give quantitative or semi-quantitative information to the analyst. Some degree of quantitation and relative quantitation is highly desirable in most post-blast cases. An ionic “profile” of post-blast samples can reveal additional information not obtained with spot tests. In the past, ion chromatography (IC) has been used as a confirmatory method to some specific wet chemical tests (4,7,10). It was desirable to obtain an independent secondary technique that has all the benefits of ion chromatography. To this end, the ATF Forensic Science Laboratory has brought on-line a Waters Capillary Ion Analyzer[™] (CIA).

Capillary electrophoresis (CE) has several advantages over IC methods, including more sensitivity, much smaller sample sizes,

and optional current-induced sampling to concentrate weak samples. Methods for the analyses of anions and cations in the examination of post-blast residues were explored and tested.

Tovex[®] and Pyrodex[®]

The cations of interest have included ammonium, potassium, calcium, and sodium because they are encountered in both low explosive mixtures primarily in the form of an oxidizing salt and in commercially manufactured high explosives. Magnesium, strontium and barium were included due to their usage in traditional pyrotechnics. In this study, the application of cation analysis by CE was expanded to include the analysis of monomethylamine (MMA) ion. MMA is added in the form of a salt, monomethylamine nitrate, in the commercial water-gel explosive Tovex[®]. An increase in the criminal use of water gel explosives, including the widely available Tovex[®] has made the detection of MMA important. Established methods of analysis for MMA include ion chromatography, thin layer chromatography (TLC) (9), and organic derivatizations followed by liquid chromatography (LC) with a nitro-specific Thermal Energy Analyzer[®] (TEA[®]) detector (5). Analysis by this CE cation method can be used as a complementary technique to IC and may eliminate the need for organic derivatizations. Moreover, this method is better suited for screening post-blast samples for the presence of Tovex[®] than other IC methods because of its improved sensitivity and shorter analysis times. Additionally, this technique can be used to detect simultaneously other cations of interest associated with Tovex[®] without chemical or instrumental modifications.

Benzoate Ions

The second part of this study expands the application of current CE anion analysis to include the analysis of benzoate ions. Sodium benzoate is added to Pyrodex[®], a commercially available modified black powder, as a fuel and burn rate modifier. Since a significant portion of pipe bombing cases involve the use of black powder or Pyrodex[®], it is advantageous to have an additional method to test for benzoate (1). The targeted anions were chloride, sulfate, nitrite, nitrate, chlorate, thiocyanate, perchlorate, and carbonate. The outlined CE anion method was used to confirm the presence of benzoate ions after detection of benzoate and cyanoguanidine by LC

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(3). The verification of Pyrodex[®] can be achieved with the detection of other anions in a specific post-blast matrix and the presence of these two additives.

CE Analysis of MMA and Benzoate

Method development for the CE analysis of both anions and cations included the selection of an electrolyte, electroosmotic flow modifiers, and buffers for each system. Extraction modifications were not explored since both the IC and the wet chemical tests use ions in DI water (18 mega-ohm) solutions. Additionally, since CE has inherent migration time shifts due to temperature, sample plug conductive interference, and sample concentration, instrumental and chemical parameters were optimized to reduce the possibility of erroneous identifications. Other methods for the identification of specific ions have relied upon spiking unknowns to verify migration times of specific analytes or were not reported (6). In order to increase the sample throughput while maintaining the integrity of identifications, several procedures were instituted.

First, as peak shifting in CE is relative, faster migrating ions were selected as reference ions. These ions were faster migrating than ions of interest. Also, both reference ions were of minimal interest to the explosives chemist. For these reasons, bromide and cesium were selected as reference ions for anion and cation analyses, respectively. Waters software references any shift in analyte migration time to the corresponding shift to the reference peak within a margin of plus/minus two percent.

Next, voltage is normally held constant in CE. However, migration of species is directly dependent upon the current, not the voltage. If there is great variability in the concentrations in the sample matrix, current (and thus migration times) will fluctuate from run to run. However, holding the current steady instead of the voltage for a short time at the onset of the analytical run will mitigate this problem. For example, a sample with 20 ppm sulfate to 1 ppm nitrate had similar migration times to a sample where the concentrations were 20 ppm nitrate and only 1 ppm sulfate.

Finally, Waters Millennium Software incorporates the average of the onset and the end of each analyte peak instead of simply using the peak apex (Table 1). This counteracted possible migration shifts due to the fronting and tailing inherent in CE when the overall electrolyte mobility did not match specific anion mobility.

Results

In this study, methods for the analysis of benzoate and MMA were developed. Benzoate and MMA ions were analyzed with standard anions and cations, respectively. This was done to determine if these ions would co-migrate or otherwise interact with the traditional ions of interest and to determine if the migration times would be in the same range as the others. It was determined that both benzoate and MMA were detectable as separate peaks. Both were detected in a reasonable amount of time without any modifications in electrolyte composition or operating parameters (Figs. 1 and 2).

Next, the practical detection limits for benzoate and MMA were determined alone and subsequently in varied complex matrices. As expected, the lower limits of practical detection were on the same order of magnitude as the other ions of interest (Figs. 3 and 4). Most other ions of interest were detectable down to low ppm or sub-ppm levels.

To ensure reliability of these methods for practical applications, samples of these ions within simulated post-blast explosive debris

TABLE 1—Parameters for cation and anion analyses using modified waters n-605 and n-601b method 2.

Cation Analysis	
Instrument	Waters Capillary Ion Analyzer TM
Software	Waters Millennium [®]
Electrolyte	Waters IonSelect TM Low Mobility Cation Electrolyte (2-hydroxyisobutyric acid, 4-methylbenzylamine, and 18-crown-6-ether)
Capillary	60 cm × 75 μm fused silica
Power supply	Positive voltage
Isomigration mode	None
Applied voltage	20 KV
Injection mode	Hydrostatic, 10 cm for 30 s
Detection	Indirect UV at 214 nm
Detector polarity	Reversed
Temperature	25°C
TIME constant	0.1 s
Sample	5 points/s
Auto purge	1.0 min with 0.1 N HCl 1.5 min with DI water 2.0 min with electrolyte
Internal standard	Cs
Extraction	DI Water
Anion Analysis	
Instrument	Waters Capillary Ion Analyzer TM
Software	Waters Millennium [®]
Electrolyte	4.3 mM sodium chromate, 0.48 mM TTAB, pH 8
Capillary	60 cm × 75 μm fused silica
Powder supply	Negative voltage
Isomigration mode	IMT5 (Waters preset mode)
Applied voltage	15 KV
Injection mode	Hydrostatic, 10 cm for 30 s
Detection	Indirect UV at 254 nm
Detector polarity	Reversed
Temperature	25°C
TIME constant	0.1 s
Sample	5 points/s
Auto purge	3 min with electrolyte
Internal standard	Br
Extraction	DI water

were analyzed (Fig. 5). Dilute samples of actual explosives were also analyzed (Fig. 6). Furthermore, single blind samples were analyzed in order to test reliability of the system for qualitative analysis (Fig. 7). These tests revealed that all ions were correctly identified in all cases. Therefore, qualitative analysis is possible using this method without additional runs with spiked analytes. Additionally, this method also allows for viewing relative ionic concentrations, as with IC, and thereby gives the explosives chemist additional information (Figs. 1 and 2).

Conclusions

Capillary electrophoresis is an effective tool in the analysis of ions from post-blast explosive debris. The Water's CIA system of chemistry and peak shift controls is adequate for qualitative analysis. The analyses of benzoate and monomethylamine ions were successfully integrated into the analysis of standard anions and cations of interest to the explosive chemist. The presence of benzoate or MMA using CE is presumptive for the presence of the commercial explosive products Pyrodex[®] and Tovex[®], respectively, and can be used as a screening technique for these explosives.

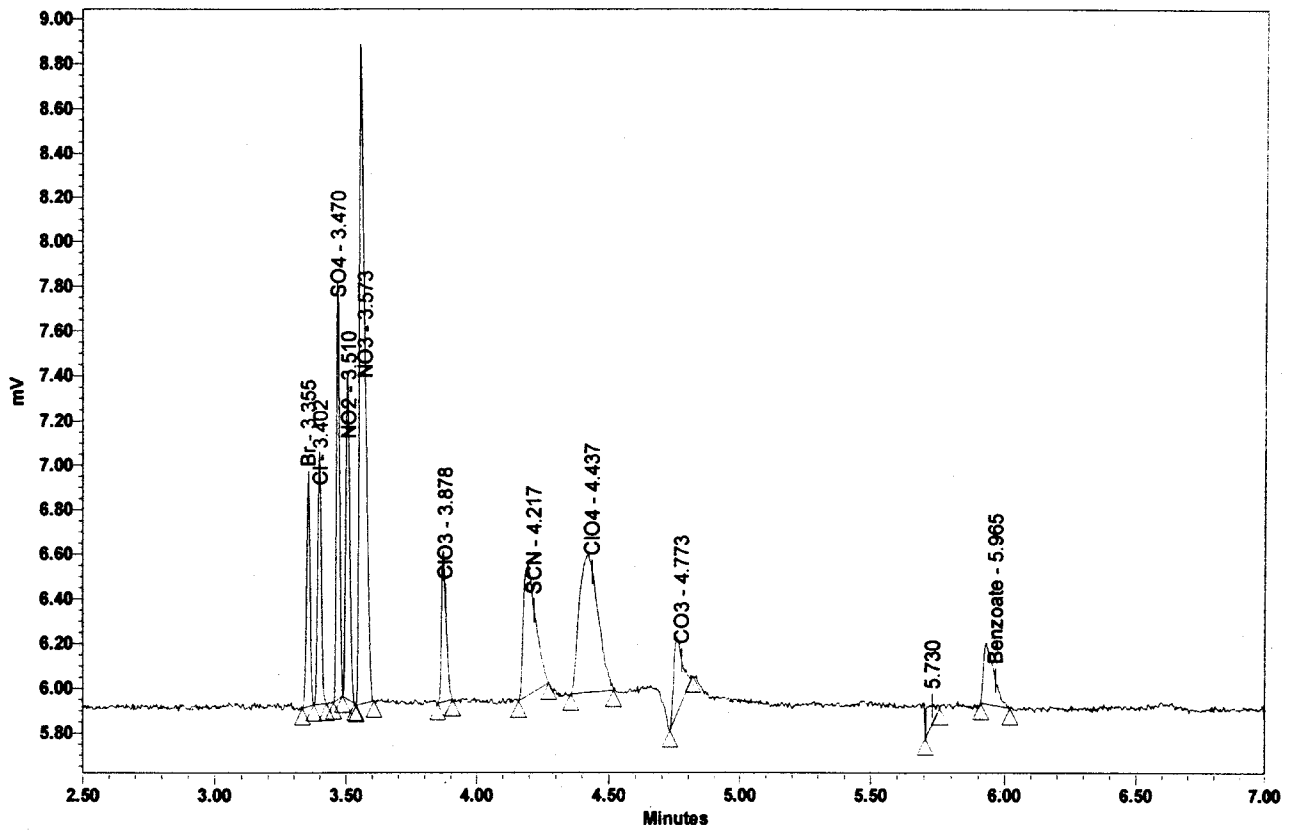


FIG. 1—Anion standard.

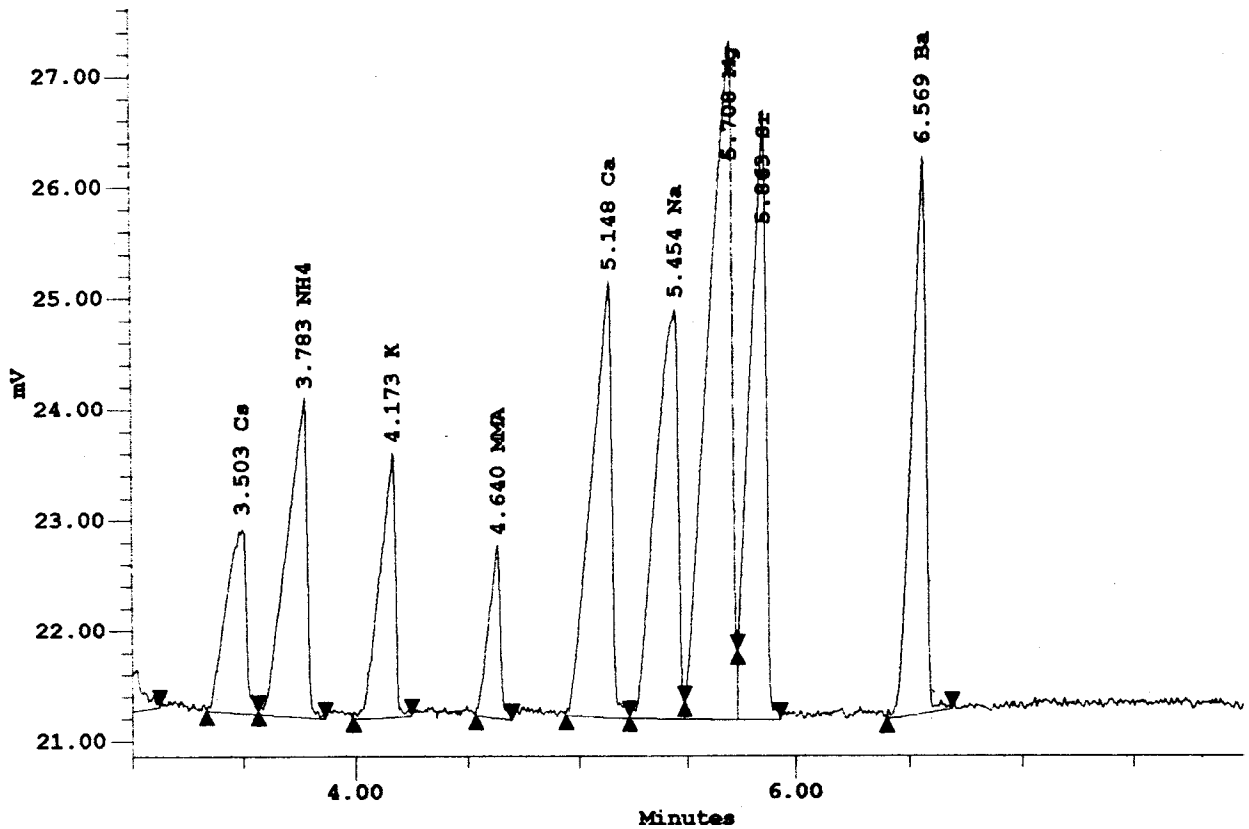


FIG. 2—Cation standard.

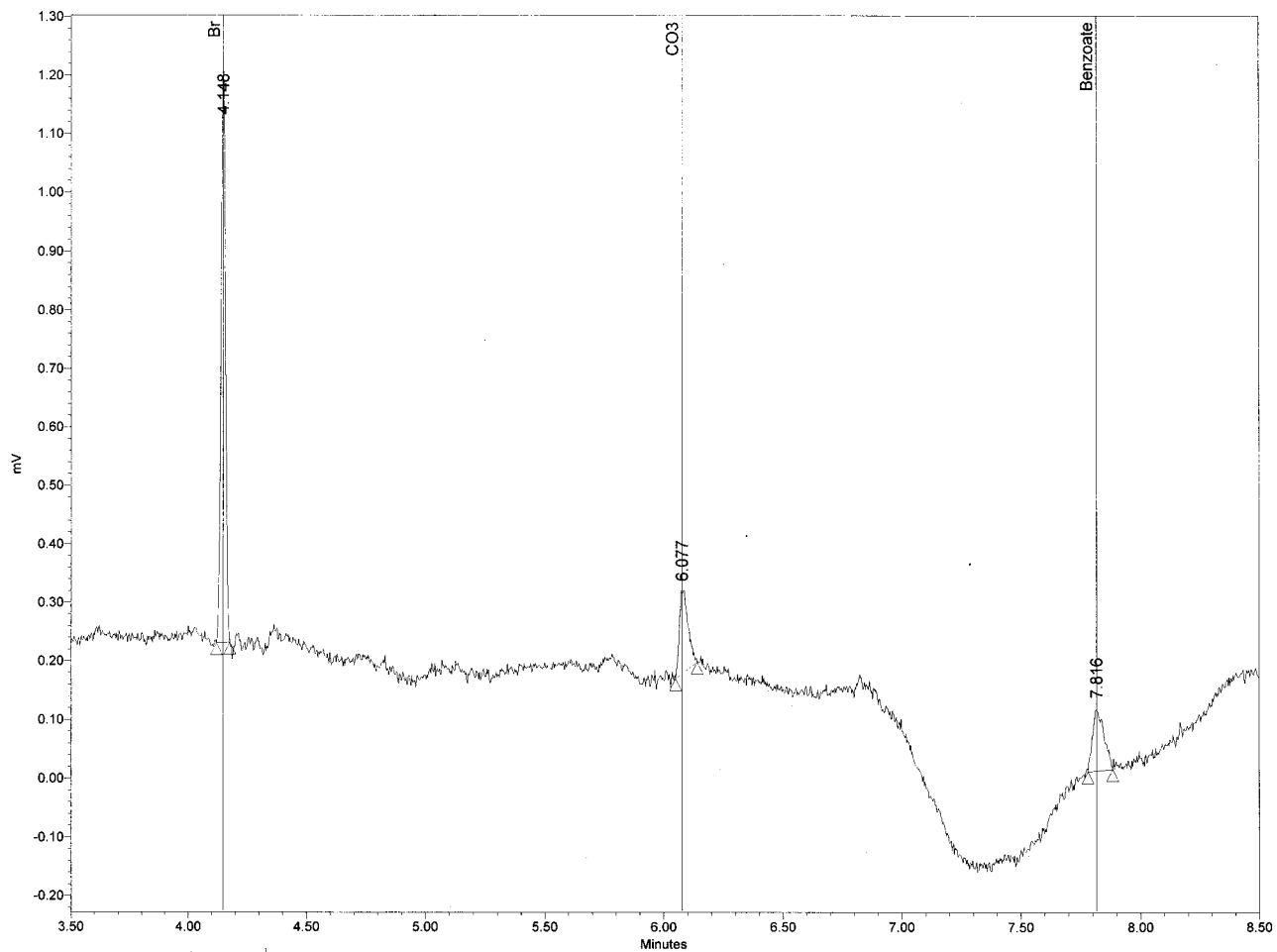


FIG. 3—1.5 ppm benzoate standard.

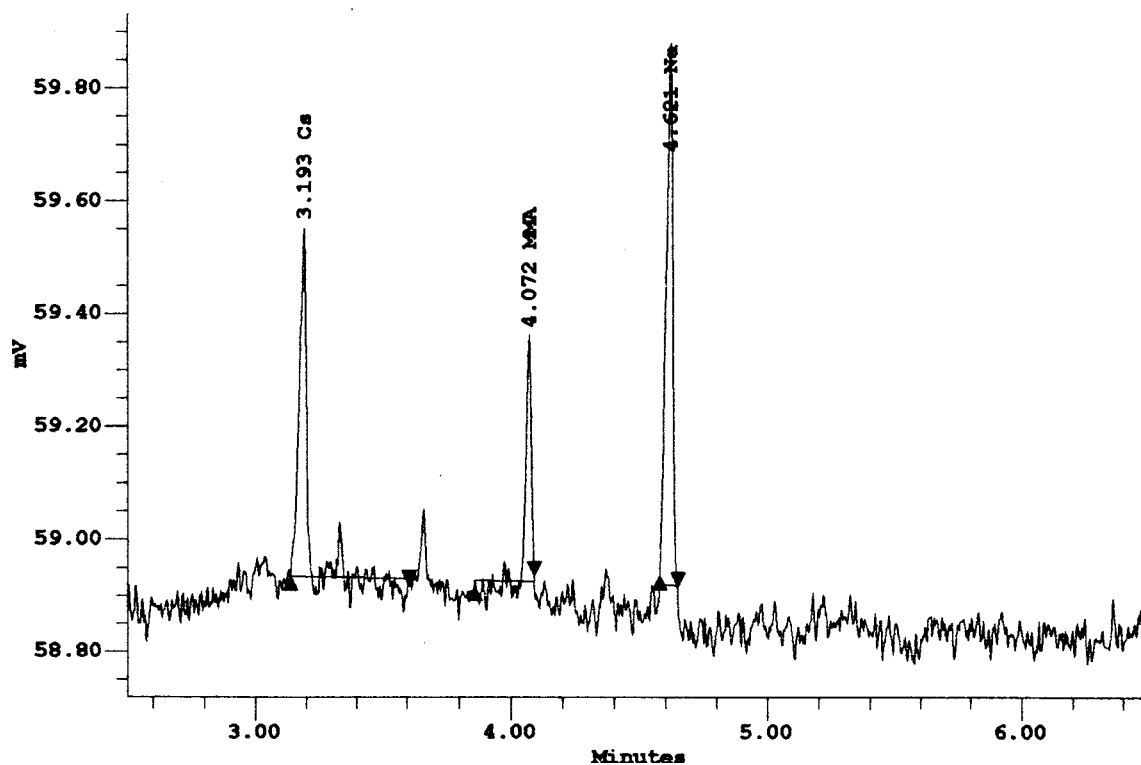


FIG. 4—200 ppb MMA standard.

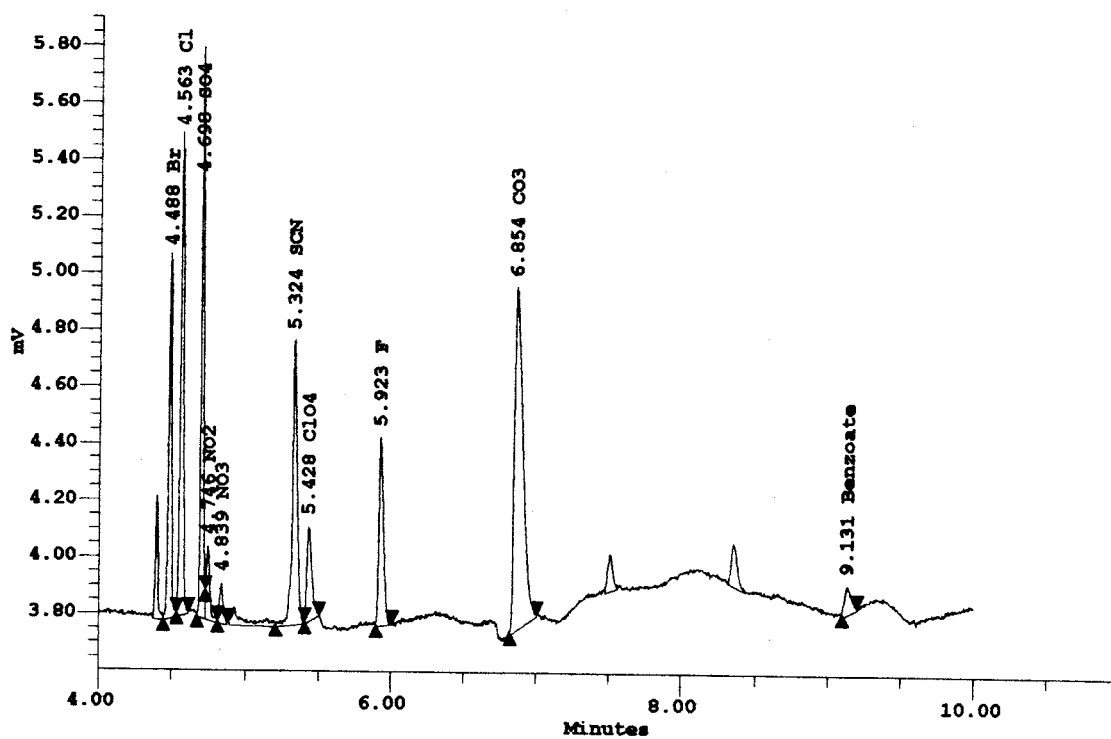


FIG. 5—Post blast pyrode.

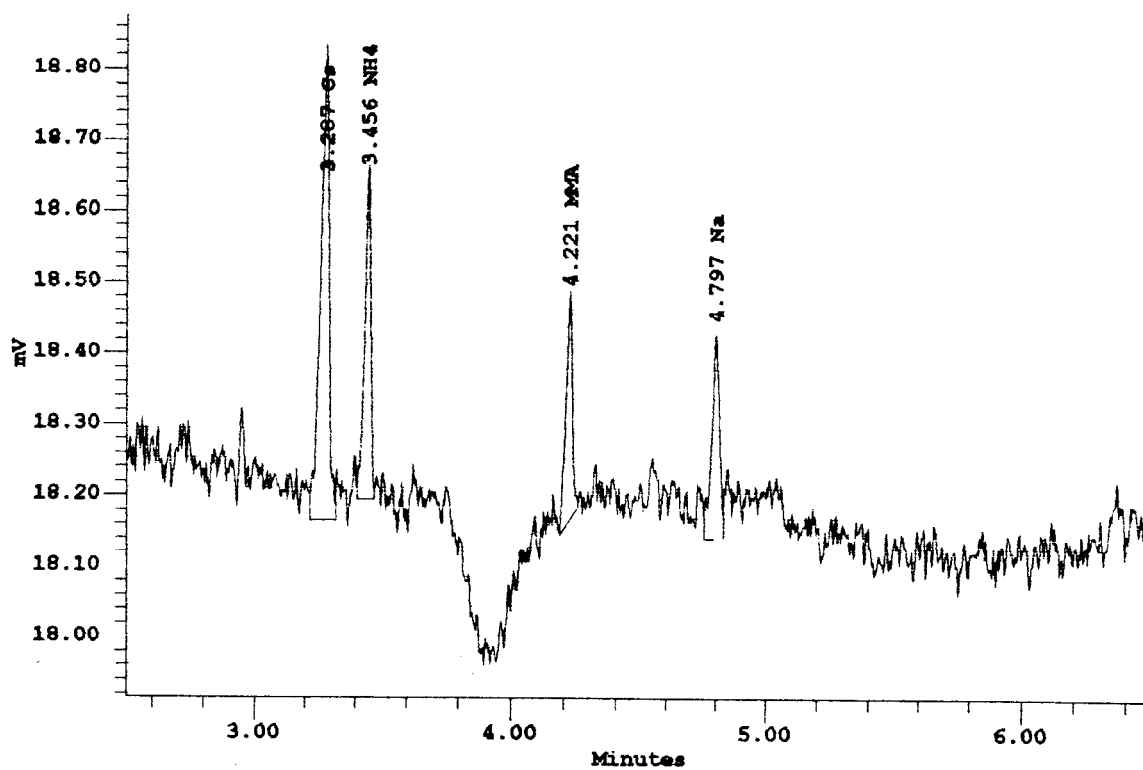


FIG. 6—Tovex.

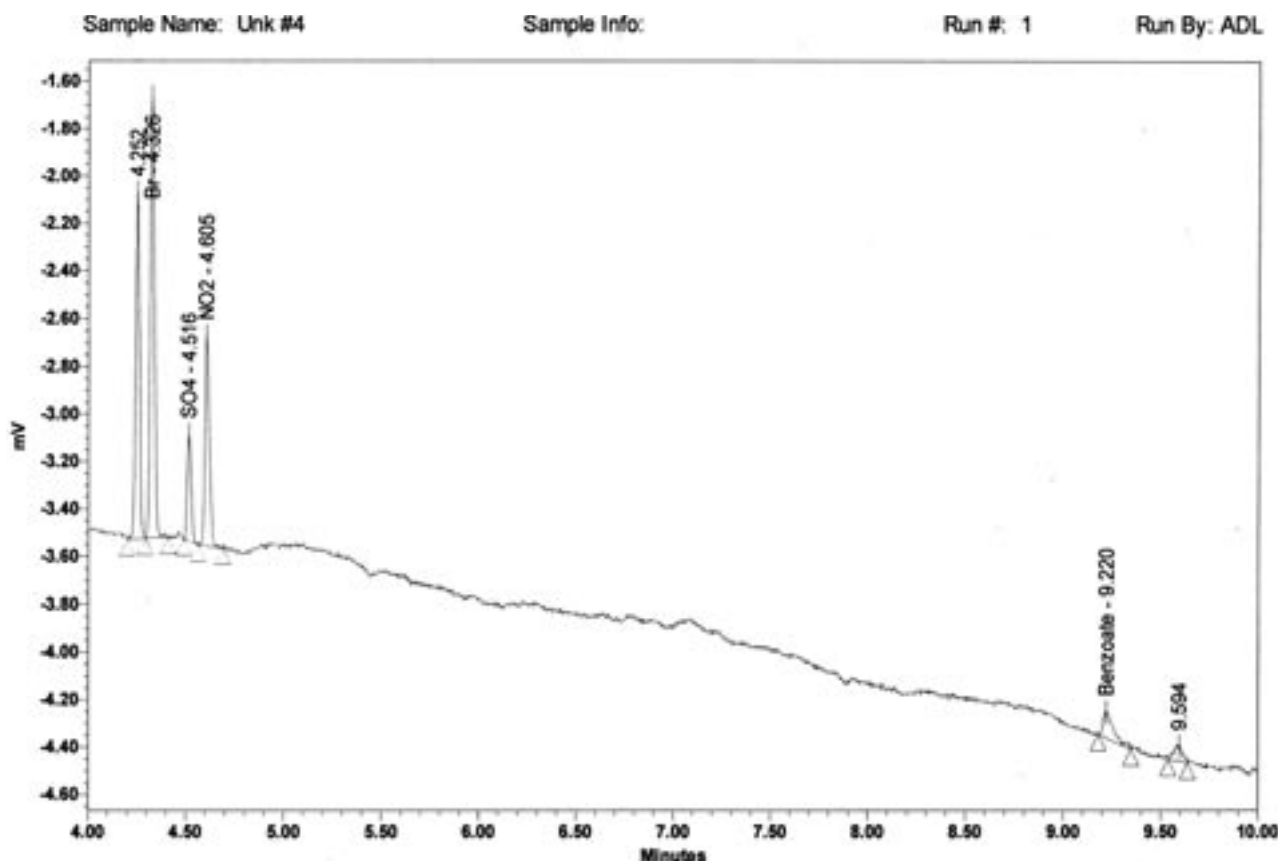


FIG. 7—Unknown #4.

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