SAND2000-0899

Diagnostic Techniques
Gas/Electrolyte/Cell Component Analysis

Rudolph G. Jungst, Ganesan Nagasubramanian, and Chris C. Crafts
MS 0613 Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185
Contact: R. G. Jungst, 505/844-1103, fax: 505/844-6972; email: rgjungs@sandia.gov

Objective:

- Understand the mechanisms of performance degradation and interactions of cell components under a variety of conditions.

Approach:

- Develop a suite of analytical techniques and postmortem analysis methods aimed at identifying the generated gas products, electrolyte breakdown products, electrode delamination, binder breakdown products, etc. The following analytical techniques are either planned to be used or will be evaluated for analysis of the reaction products or breakdown of cell components:
  1) For gas analyses: GC, GC/MS, etc.
  2) For electrolyte decomposition: IC, GC/MS
  3) For cathode or current collector dissolution: ICP-MS
  4) Electrode delamination: visual inspection
  5) Separator breakdown: flow porometry
  6) Binder breakdown: GPC

Accomplishments:

- A procedure for punching 18650 cells and collecting headspace gas samples for analysis was developed and successfully tested on both Sony cells and Gen1 ATD cells.
- Electrolyte samples were successfully collected from Sony cells and Gen1 ATD baseline cells.
- A new procedure was developed that makes possible the analysis of $LiPF_6$ electrolyte salt concentrations for the first time on aged cells. The method also is able to quantitatively determine fluoride, which is an expected salt decomposition product.
- The electrolyte solvents were also analyzed by GC/MS and library spectra were collected for the baseline constituents.
- Inductively coupled plasma-mass spectroscopy has been demonstrated to have very high sensitivity for metallic species in lithium-ion cell electrolyte or in solid electrode material. Baseline analyses of both electrolyte and electrodes have been successfully carried out, showing a variety of metals in the 1 – 300 ppm range for the electrolyte.
- A procedure for postmortem of 18650 lithium-ion cells and recovery of samples of the cell components for analysis has been developed. The postmortem procedure has been written up and shared with other members of the ATD team. Delamination of

the cathode from the aluminum current collector was observed in thermally aged Sony cells during a postmortem.

Future Activity:

- The analytical methods that have been developed successfully will be further tested using aged Sony cells.
- Feasibility evaluations will be completed on techniques to detect separator breakdown and binder breakdown.
- Optimized analytical methods will be implemented on the Gen1 cells as diagnostic samples become available.

The Sandia Analytical Laboratory has supported the ATD program by providing analytical services through performing headspace gas sampling and analysis, electrolyte analysis for organic and inorganic constituents, and inorganic analysis of cathode and anode materials. Specialized methods for determining the electrolyte salt concentration were developed by members of the Explosive Materials/Subsystems Department. Postmortems of lithium-ion cells and collection of component samples were done by the Sandia Lithium Battery R&D Department.

Headspace Gas Analysis.

Headspace gas analysis is performed by placing an 18650 lithium-ion cell in a puncture fixture (Figure 1) that may be attached to a gas chromatograph (GC) or gas chromatograph/mass spectrometer (GC/MS). This unique gas sampling capability has evolved from earlier work at Sandia on decomposition of organic explosives in small, sealed components. After puncturing the cell, headspace gases may then be analyzed for organic and inorganic gases by gas chromatography. Typical chromatograms for inorganic and organic gases collected from Sony cells and a Gen1 ATD cell are shown in Figures 2 and 3. By the puncturing and analysis of cells that have had differing conditions of thermal aging or abuse imposed on them, it will be possible to build a picture of the decomposition products in the cell headspace and hence the relative amount of decomposition and reaction of cell components.

Figure 1. Cell Headspace Sampling Fixture

Figure 2. Headspace Gas Analysis – Sony Cells

Figure 3. Headspace Gas Analysis – Generation 1 Baseline ATD Cell

Electrolyte Decomposition

Decomposition of the electrolyte in lithium-ion cells is followed by two primary analytical methods, ion chromatography (IC) and gas chromatography/mass spectrometry (GC/MS). In order to perform this analysis, it is necessary to collect a sample of electrolyte from the cell. A method for centrifuging a punctured cell has been developed that allows collection of several tenths of a ml of solvent without exposing the sample to air. This sample is then split for analysis of the electrolyte salt, electrolyte solvent, and dissolved metals.

The $LiPF_6$ electrolyte salt is analyzed using a specialized IC method developed for the ATD program. Both PF_6^- and F^- are quantified in a single run from a 40-microliter sample of the electrolyte. Figure 4 shows a sample chromatogram. A calibration curve has been constructed for PF_6^- (Figure 5) and the instrumental response is shown to be linear over a wide range of concentration. The sensitivity for F^- by this method is also good with a detection limit of as little as 6.6 mM in the undiluted electrolyte.

Figure 4. Ion Chromatogram of a Battery Electrolyte Sample

Figure 5. Calibration Curve for PF_6^- Determination by Ion Chromatography

Electrolyte solvents in the spun out sample are analyzed by standard GC/MS technique. A number of common electrolyte solvents have been analyzed to accumulate a mass spectral library for these materials. Samples from two generation 1 ATD cells were also analyzed to confirm the electrolyte composition and to look for trace levels of impurities.

Cathode or Current Collector Dissolution

Analysis of the cathode and anode materials and electrolyte by inductively coupled plasma/mass spectrometry (ICP/MS) enables the composition of these cell components to be tracked after various abuse treatments have been applied. The primary species of interest relate to the migration of metals from the cathode active material or from the current collectors to other parts of the cell. It is also possible to determine the lithium content and migration into the cathode and anode materials by using this method. Sample preparation is relatively simple for electrolyte, where the liquid is simply diluted with 2.5% nitric acid. Solid electrode samples must be dissolved in nitric acid using high-pressure digestion. Analysis of electrolyte from two baseline Gen1 ATD cells showed generally low levels of metals. Average values found for the metals of most interest were: Al – 25.2 ppm, Cu – 10 ppm, and Ni – 204 ppm. These two cells were run through a forced discharge test prior to recovery of the electrolyte, but no venting or significant heating had occurred. Additional samples will be collected and tested in the future from cells subjected to life or thermal abuse tests in order to determine if the metallic impurity levels are rising.

Separator and Binder Breakdown

Feasibility tests for methods to detect changes in the separator and electrode binder have not yet been carried out, but are planned for the future. Separator porosity is influenced by elevated temperature and complete shutdown should occur in the vicinity of 120 – 130°C. Characterization of the pore size of the separator can be done by using flow porometry and a trial measurement will be carried out in the near future to demonstrate this capability. If a favorable result is obtained, then flow porometry measurements will subsequently be made on material recovered from aged or thermally abused cells to find out if the separator porosity is changing.

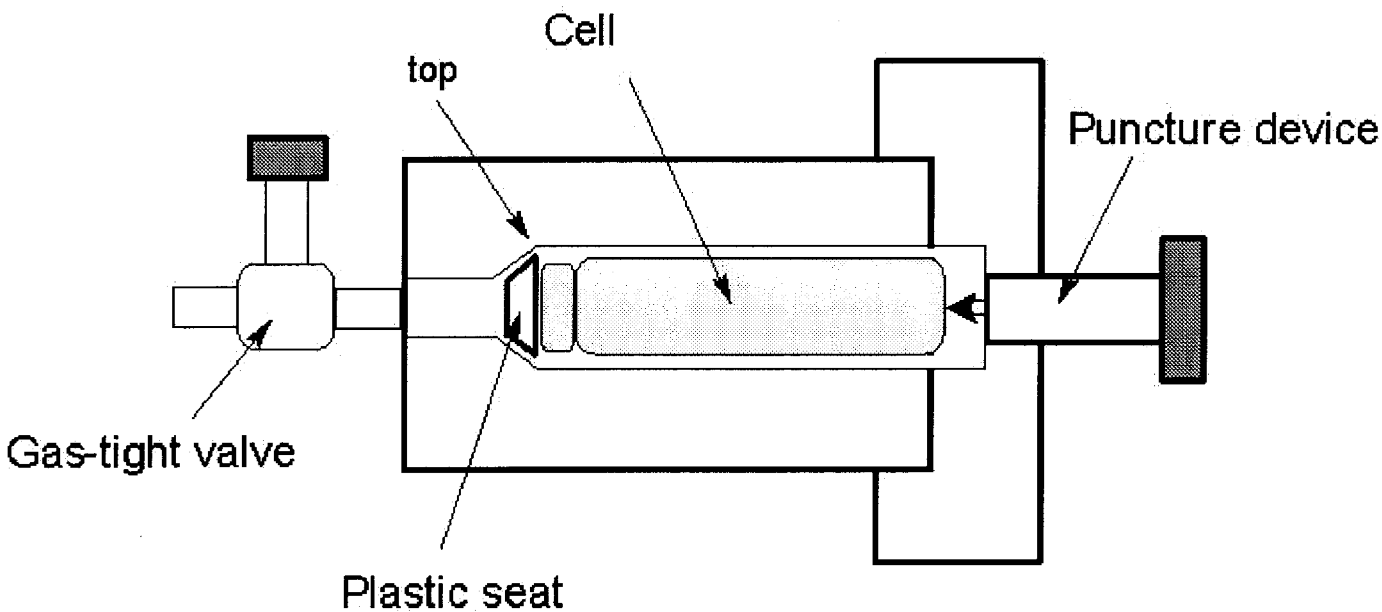
Breakdown of the polymeric structure of the binder should be detectable by dissolving the PVDF from an electrode and analyzing the material by gel permeation chromatography (GPC). Equipment to perform this test is available at Sandia and we will soon be sending an analyst to receive training on this method. Once this training has been completed, a feasibility trial will be performed.

Future Work

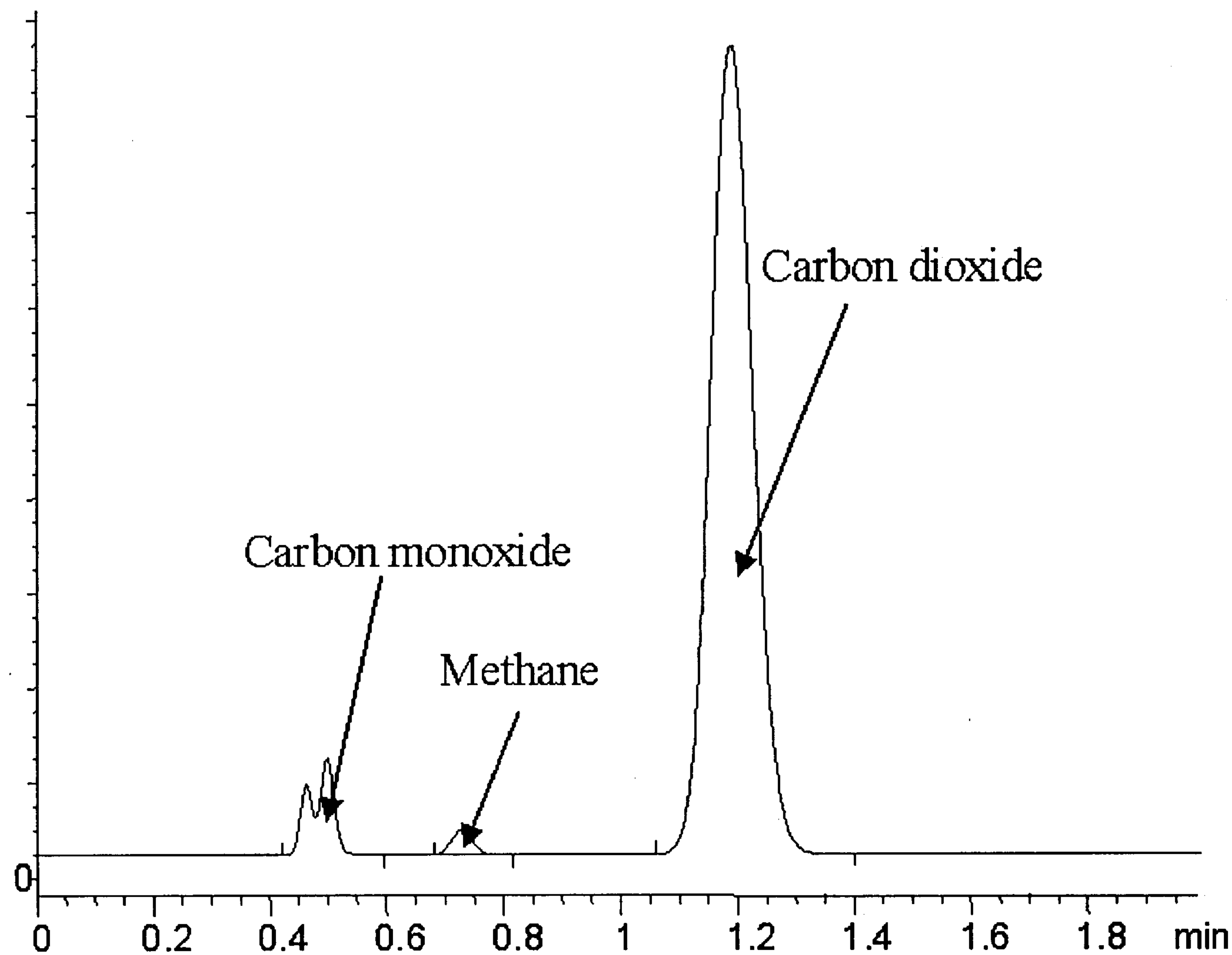
Most of the analysis procedures have already been developed, so future work revolves mainly around applying them to diagnostics cells from the ATD life tests. A small number of Sony lithium-ion cells have been put through a trial version of the life test matrix, and these samples will provide a final opportunity to test the analytical protocols. Procedures for studying the breakdown of the separator and binder are not completely defined at this point, but this area is being addressed. The major effort in the diagnostics area will be applying the developed techniques to analysis of the Gen1 ATD cells after they have been subjected to life testing.

Acknowledgements

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000. We are grateful to the following individuals for performing the indicated analyses: T. T. Borek (GC/MS), S. E. Klassen and E. P. Boespflug (IC), J. E. Reich (ICP-MS), M. J. Russell (cell postmortem), and H. L. Case (sample collection and distribution).



Cell
top
Puncture device
Gas-tight valve
Plastic seat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Carbon monoxide
Methane
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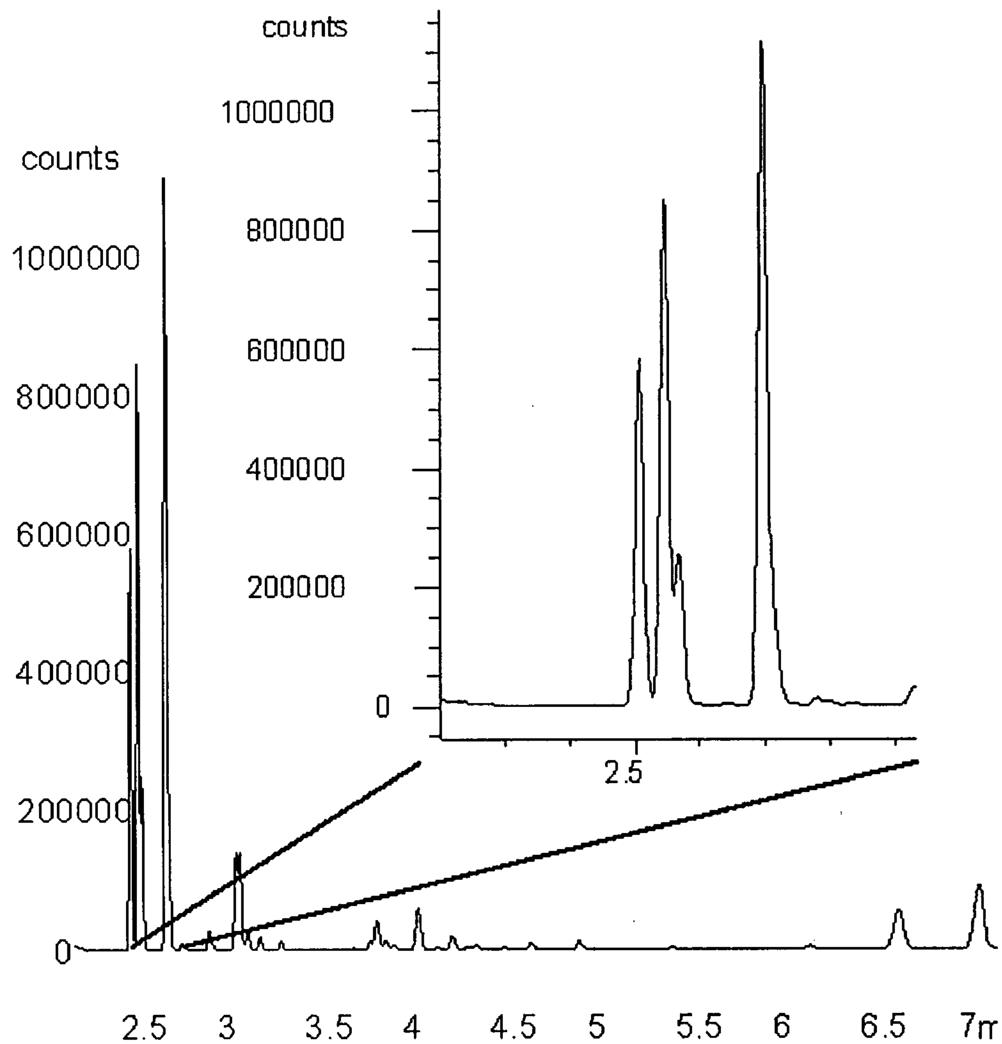
1.4
1.6
1.8
min



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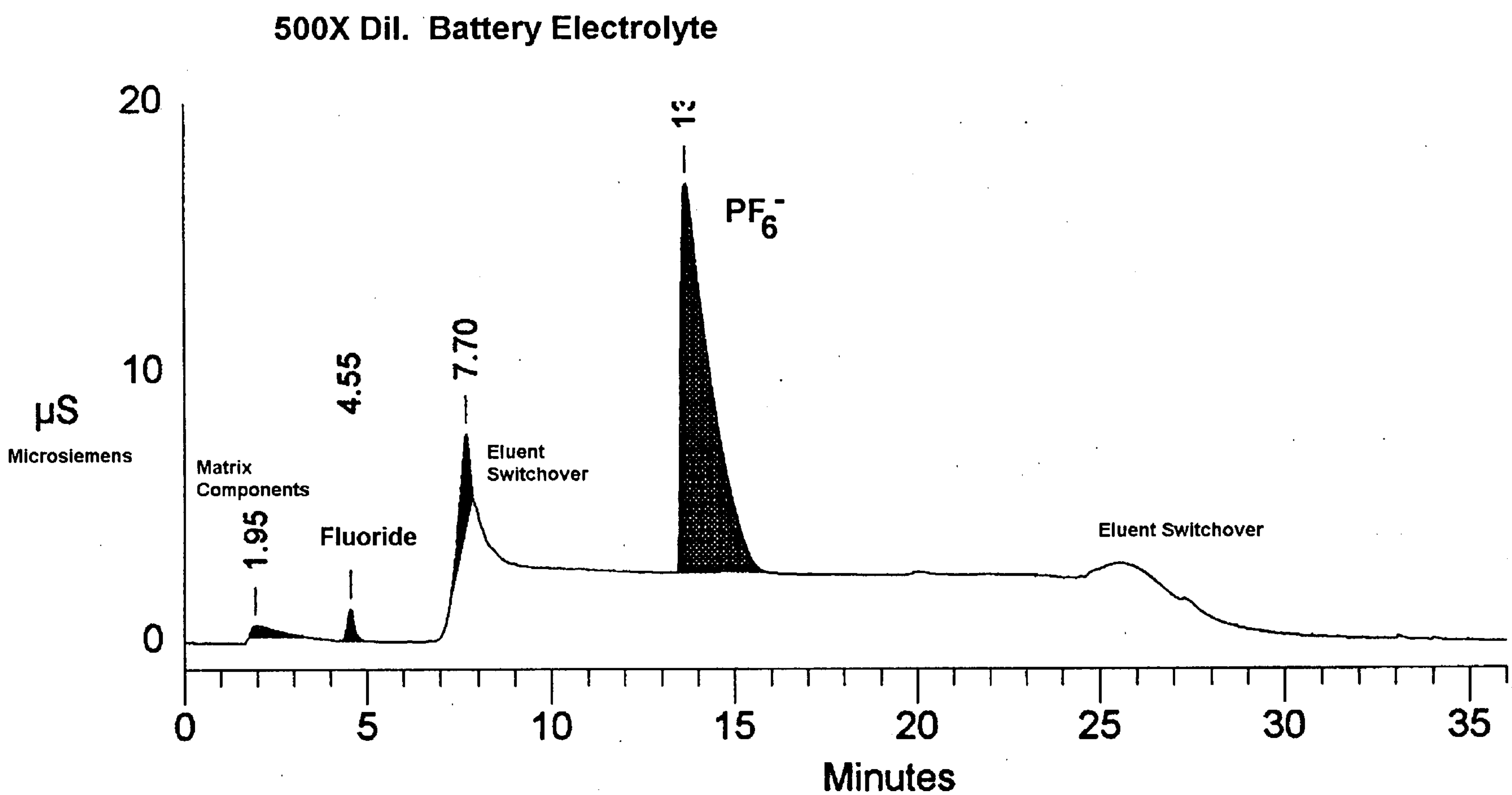
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Microsiemens
Matrix
Components
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Fluoride
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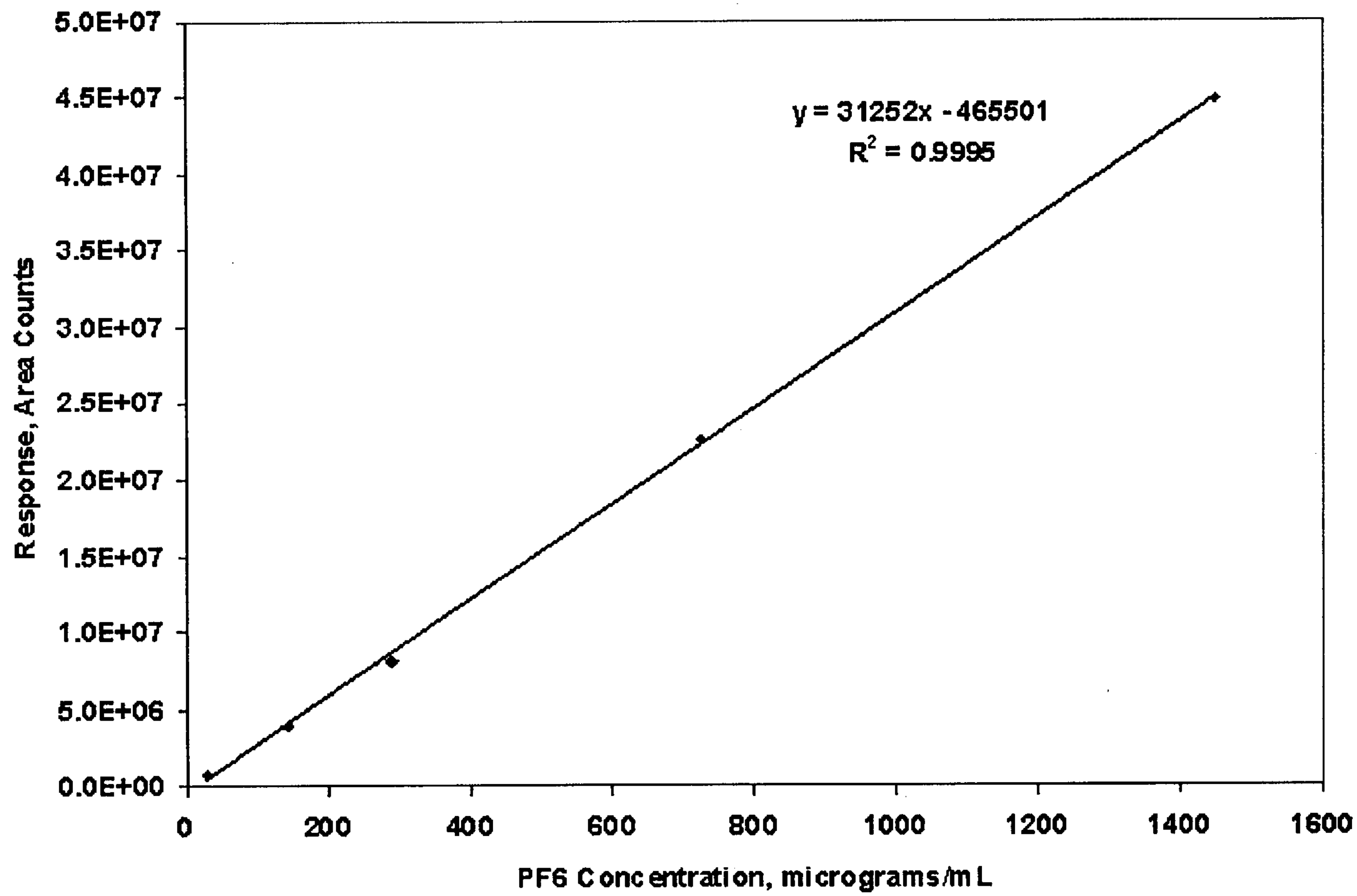
7.70
Eluent
Switchover
13
PF6-
Eluent Switchover
0
5
10
15
20
25
30
35
Minutes



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1.5E+07
1.0E+07
5.0E+06
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0
200
400
600
800
1000
1200
1400
1600
PF6 Concentration, micrograms/mL