I. Scope

IC/MS is used for the identification of inorganic monatomic and polyatomic ions and organic acids commonly found in explosives and their combustion products. Typically this includes compounds with molecular weights less than 200 amu. IC/MS can be used to analyze extracts of both intact explosives and post blast evidence.

This Standard Operating Procedure covers the application of electrospray IC/MS to the analysis of low explosives, oxidizers and other inorganic/organic materials related to explosive casework (e.g., unknown chemicals and extracted components of explosive devices) at ATF.

II. References:

Surveyor MSQ Hardware Manual, Revision B, Thermo-Finnigan

Advances in Atmospheric Pressure Ionization (API) LC/MS and GC/MS Methods of Analysis and Detection of Explosives, Peter A. Dreifuss and Katherine Klontz Proceedings of the 7th International Symposium on the Analysis and Detection of Explosives, pp. 258- 272, 2001.

Determination of Perchlorate at Trace Levels in Drinking Water by Ion-Pair Extraction with Electrospray Ionization Mass Spectrometry, Matthew L. Magnuson, Edward T. Urbansky and Catherine Kelty, Analytical Chemistry, Vol. 72, No. 1, January 1, 2000.

Determination of Perchlorate in Environmental Waters by Ion Chromatography Coupled with Electrospray Mass Spectrometry (IC-MS), Dionex Corporation, Application Note 151.

IC-MS Determination of Ionic Compounds in Toothpaste, Silvano Cavalli, Heiko Herrmann and Frank Hofler, LC/GC Europe, 17(3), 160-165 (2004).

The Analysis of Perchlorate by Ion Chromatography/Mass Spectrometry, Johnson Mathew, Jay Gandhi, Joe Hendrick, Agilent Technologies, Application Note 5989-0816EN

III. Apparatus/Reagents:

Reference IC/MS Operating Parameter Sheets for specifics concerning the IC/MS Instrumentation.

IC/MS conditions: Reference IC/MS Operating Parameter Sheets for specifics concerning the IC/MS conditions. A parameter sheet will be present in each case jacket that includes IC-MS data.

IV. Safety Precautions:

- Pump exhaust should be vented to a fume hood or other vent whenever facilities permit.
- Used pump oil may contain chemicals that could pose potential health hazards and should be disposed of in a safe manner; e.g., Safety Kleen or other vendor. Operators changing oil should wear laboratory coats, protective gloves and protective eyewear.
- All gases should be properly secured/stored. Pressure regulators should be inspected whenever the cylinders are replaced.
- Any maintenance or inspection of electrical circuits is to be limited to the primary operators familiar with the specific hazards. Whenever possible the work should be done in the company of a "buddy".
- The hazards of chemicals and solvents must be understood before working with them.

V. Procedures:

- Tuning and Calibration - The mass spectrometer should be tuned and calibrated annually, or as necessary, by the primary operator, secondary operator, or the primary operator's designee. This is accomplished with a calibrant consisting of 50 ng/µL of sodium iodide in 50:50 (v/v) isopropyl alcohol/water in a mobile phase of 50/50 acetonitrile/water. Calibration documentation consisting of the Auto Tune Report should be placed into the instrument logbook and initialed by the primary operator conducting the tune.
- Acceptable conditions - As a minimum verification of the adequacy of the tuning and calibration, a standard will be analyzed and the data evaluated. The standard component peaks should show peak height, shape & resolution comparable to the previously run standard. The IC/MS system can be used for the analysis of samples only after good quality spectra of the targeted species can be produced. Good quality spectra can be defined as mass spectra with sufficient response that allows for determination of a peak above the baseline noise, usually a 3:1 signal to noise ratio, that allows for the identification of the mass or masses contained within that peak without interference from masses not associated with that compound.
- Sample Analysis
    1. Every time the IC/MS is used, the examiner's name, date, and case number, at a minimum, will be recorded in the logbook.
    2. Each sample set should include a materials control, which is representative of all the procedures used in preparing the sample.
    3. Water blanks should be run immediately before a standard, materials control, or sample extract (with the exception of the sample following a clean materials control).
    4. Sample concentrations should be checked with a conductivity meter prior to analysis, and diluted as necessary.
    5. Samples must be prepared using deionized water having a resistivity of 18.0 MegaOhms or higher, disposable plasticware (i.e., plastic beakers, pipets, syringes), and disposable IC-specific filter cartridges.

The following ions are characteristic of the listed components:

Component	Characteristic Ions (m/z)
Chloride	35, 37*
Nitrite	46, 62
Sulfate	97, 99*
Nitrate	62, 46
Chlorate	83, 85*
Benzoate	121
Phosphate	79, 97
Thiosulfate	113, 112, 80, 115*
3-nitrobenzoate	166, 122, 46
Thiocyanate	58
Perchlorate	99, 101*

Note to Table: *- represents isotopic ions

An IC/MS sample analysis will be designated as positive for the presence of a specific inorganic ion or other targeted material if the background-subtracted mass spectrum of the component is consistent with that of the standard material and the retention time agrees within 5%. Due to the greater sensitivity of the MSQ over the conductivity detector for some ionic components, an extracted ion profile with a retention time within 5% of that of the standard, in addition to an identifiable mass spectrum are sufficient for identification. Furthermore, the water blank or control immediately preceding the sample must be acceptable. It must also be noted that due to the inherent sensitivity of the Anion IC/MS method, trace amounts of ions such as sulfate and chloride may be detected in water blanks. The background levels of these ions must be taken into consideration when making identifications.

d. Instrument and Periodic Maintenance: All instrument maintenance necessary for proper instrument performance will be documented in an instrument maintenance log. The log will also document the maintenance and symptoms from any electrical component failures that might occur.

e. Non-routine exam – allowance for variation: Changes to any of the IC/MS methods may be necessary for unique examinations of ionic species that may not be normally encountered yet need to be examined for a given case. Columns, eluents, and instrumental parameters may be changed to perform a unique analysis. Any such changes must be fully documented.

VI. Quality Assurance/Quality Control:

a. Logs must be maintained as to operator use.
b. Logs must be maintained as to standards.
c. Logs of service/maintenance must be maintained, both in-lab, and vendor service.
d. Primary Operators should perform and record maintenance to correct any of the following:
    - Loss of resolution
    - Loss of retention
    - Loss of detector response

- Abnormal peak shapes
- Abnormal operating pressures

e. Possible sources of Error:

Possible sources of MS error include impurities from solvents and/or carryover from prior analyses. Other possible sources of error include calibration errors and gradual de-tuning of the instrument, which normally do not contribute to the generation of false positives. These sources can be entirely eliminated through the analysis of standards, blanks and materials controls. Also, temperature and sample concentration may have an effect on retention time and chromatographic separation. This is addressed by keeping the column compartment at a constant temperature, and by diluting samples prior to analysis. Environmental - The increased sensitivity and the ability to confirm trace levels of materials necessitate a level of awareness of anions that are commonly found in the environment at trace levels.

Other - Reference the IC/MS documentation for more information on the sources of error for mass spectrometers.

Glossary

Calibration – electronic adjustment of a mass spectrometer's analyzer to measure the correct m/z values.

Extracted Ion Profile – a reconstructed chromatogram of a selected mass-to-charge ratio (m/z).

False positive - a spectral response originating from the instrument, solvent, sample extraction or otherwise originating from sample workup.

Ionic mass or formula weight - terms used for the mass of the intact ion calculated from the mass of the most abundant isotope of each element present. We use these terms in place of molecular weight since the analytes are not molecules.

Mass Spectrum – a plot of ion abundance versus mass-to-charge ratio for a single mass spectrometer scan or series of scans, reflecting scan summation or background subtraction.

Materials Control – a sample prepared for analysis using the same procedures used in preparing a forensic exhibit. Analysis of this sample and demonstration that an analyte is not detected, precludes the possibility of a false positive.

Quadrupole - a common mass analyzer used in mass spectrometry to analyze the mass-to-charge ratio (m/z) of ions produced in the ion source. The quadrupole consists of four metal rods which carry radio frequency and DC voltage which are varied in such a way to sequentially and rapidly transmit ions of known mass.

Retention Time - the time which it takes a component to travel through the IC system.

Tune – adjustment of mass spectrometer lens voltages and other parameters to maximize and normalize ion production, transmission and detection.