10.13 Solvent Analysis / Reagent Analysis

Clandestine Drug Laboratory or Other Solvent or Reagent Analysis / Identification - Introduction:

Solvent analysis pertains to various different chemical solvents that may be submitted to the laboratory. These may be submitted as general unknowns or as suspected solvents utilized in the production of drugs.

Laboratory personnel are often incorporated in support investigations of clandestine drug laboratories by the analysis of non-drug samples for the presence of chemical reagents utilized in the manufacture of controlled substances. Analysts are often called upon to identify the chemical reagents and/or the chemical solvents that may be submitted to the forensic laboratory. These chemical reagents and/or chemical solvents may be submitted as general unknowns or as suspected solvents utilized in the production/manufacture of drugs.

10.13.1 Clandestine Laboratory Chemical Solvent Analysis

There are many types of chemical reagents which can be utilized in the production of Methamphetamine. Often, it is requested by the submitting agency or the prosecutor to identify particular chemical reagents and/or chemical solvents.

10.13.1.1 Safety Considerations

Chemicals used are flammable. Use in fume hood.

10.13.1.2 Preparations

Materials needed:

- Gas tight needle and syringe (2 ml max.)
- Appropriate control standards

10.13.1.3 Instrumentation: Gas Chromatograph - Mass Spectrophotometer

Suggested Instrument Parameters (Headspace and CS2 Dilution):

Carrier: He or H2

Splitless

Air: 300 ml/min.

Carrier gas: 30 ml/min.

Range: 10-12A/MV

Injector: 225º C

Detector: 275º C

Carrier flow: 2.0 ml/min.

Suggested Program Parameters:

Headspace:

Initial: 40º for 4 min.

Ramp: 25º/min. to 250ºC

CS2 Dilution:

Initial: 40º for 3.7 min.

Ramp: 12º/min. to 100ºC

Ramp: 20º/min. to 280º

Hold: 5 min. at 280ºC

10.13.1.4 Minimum Standards & Controls

A standard control solvent comparable to the unknown solvent and air/solvent blanks.
GC-MS minimum standards and controls. *See 7.7 Gas Chromatography - Mass Spectrometer (GC-MS)*

10.13.1.5 Procedure or Analysis

Headspace:

- Set the run conditions for the GC-MS
- Run an air blank sample (volume of between 1ml and 1.5ml)
- Extract a headspace sample from the unknown solvent of between 1ml and 1.5ml
- Inject the sample into the GC-MS and begin analysis
- For cases with multiple samples, an air blank must be run between each sample

- Compare unknown solvent data with known solvent standards using retention time and mass spectra

CS2 Dilution:

- Set the run conditions for the GC-MS
- Run a system CS2
- Prepare a diluted unknown sample with CS2 by adding 20ul of unknown to 2ml of CS2
- Inject sample into the GC-MS and begin analysis
- For cases with multiple samples, a CS2 blank must be run between each sample
- Compare unknown solvent data with known solvent standards and mass spectra

10.13.1.6 Instrumentation: FTIR

Some solvents can be identified utilizing the FTIR; Compare to known reference samples prepared in the same manner (ex: gas cell or liquid cell). Also see "10.13.2.2.1 Fourier Transform Infrared Spectrometer (FTIR)" below.

10.13.1.7 Interpretation and Report Wording

Explanation of Terms Used in Report:

The following descriptions are meant to provide context to the levels of opinions reached in the report.

Identification: The sample contained an organic solvent or residues of an organic solvent.

Not Identified: No definitive conclusion could be reached regarding the presence or the absence of an organic solvent in the sample. Insufficient data exist to support identification of an organic solvent, if present. Possible factors leading to insufficient data include but are not limited to:

- Degraded liquids (evaporation, bacterial degradation)
- Insufficient concentration of an organic solvent or component(s)
- Unexplained absence of components compared to a reference liquid
- Unexplained differences in ratios of compound types (aromatics, alkanes, etc.) compared to a reference liquid
- No comparable sample in reference collection
- Interfering compounds from the sample

Not Detected: No indications of an organic solvent in the sample were present.

10.13.2 Clandestine Laboratory Chemical Reagent Analysis

10.13.2.1 Safety Considerations

Standard chemical laboratory handling practices should be followed. See FSD Safety Manual

10.13.2.2 Instrumentation:

10.13.2.2.1 Fourier Transform Infrared Spectrometer (FTIR)

10.13.2.2.1.1 Introduction

FTIR alone or in combination with other analytical techniques may be used for positive identification of a chemical compound or chemical mixture.

10.13.2.2.1.2 Safety Considerations

If utilizing the microscope attachment, the detector uses liquid nitrogen. Care must be used to protect the eyes and skin while working with liquid nitrogen.

10.13.2.2.1.3 Preparations

Tools for sampling and sample manipulation.

10.13.2.2.1.4 FTIR Analysis

The questioned sample will dictate the method of analysis on the FTIR, such as ATR, bench, microscope, etc. Compare IR spectra obtained from unknown powders and/or residues to known IR spectra from known powders and/or residues. A spectrum library search can aid the analyst in identifying an unknown powder and/or residue.

10.13.2.2.1.5 Minimum Standards and Controls

Perform appropriate FTIR function verifications. Compare spectra to known IR spectra from known powders and/or residues and include those in the case record.

10.13.2.2.1.6 References

Keto, R.O. "Improved Method for the Analysis of the Military Explosive Composition C-4"; Journal of Forensic Sciences, 1986, 31, 1, 241-249.

Miller, F.A.; Wilkins, C.H. "Infrared Spectra and Characteristic Frequencies of Inorganic Ions"; Analytical Chemistry, 1952, 24, 1253-1294.

Pristera, F.; Halek, M.; Castelli, A.; Fredericks, W. "Analysis of Explosives using Infrared Spectroscopy"; Analytical Chemistry, 1960, 32, 2, 495-508.

10.13.2.2.2 Ion Chromatography (IC)

10.13.2.2.2.1 Introduction

Ion Chromatography is used to separate and subsequently identify anions and cations present in a sample by comparison of retention times.

10.13.2.2.2.2 Safety Considerations

See FSD Safety Manual

10.13.2.2.2.3 Preparations

Samples should be prepared using deionized reagent grade water as the solvent. It may be useful to heat the reagent grade water prior to analysis. Reagent grade water blanks must be run between samples. A standard mix of anions and/or cations must be run prior to the questioned samples.

10.13.2.2.2.4 Minimum Standards and Controls:

Ion chromatograph (with autosampler if desired).

The **"Total Conductivity"** and **"Pressure"** for each system used shall be recorded (instrument log book or electronic file near/on the instrument) on a regular basis and should be recorded prior to use each day the instrument is run.

An Anion standard mixture sample and/or Cation standard mixture sample shall be run each day of each system's use.

Reagent grade water blanks must be run between samples.

10.13.2.2.2.5 Anion System 1 and System 2 – Suggested Parameters:

Note: Standard mixture for Systems 1 and 2: fluoride, chloride, nitrite, bromide, chlorate, nitrate, phosphate, sulfate, iodine, perchlorate (perchlorate not detected on System 1)

Anion - System 1

COLUMNS:

Column:	Diones IonPac AS9-HC 4 x 250mm
Guard column:	DIONEX IonPac AG9-HC 4 x 50mm
Suppressor:	ASRS 300 4mm
setting:	54 mA
Detector:	Thermo conductivity detector
Flow rate:	1.200 ml/min
Mobile Phase:	9 mM sodium carbonate (Na_2CO_3)
Gradient:	Isocratic
Injection Loop Volume:	25ul

Anion with perchlorate – System 2

COLUMNS:

Column:	Dionex IonPac AS19 4 x 250mm
Guard column:	Dionex IonPac AG19, 4 x 50mm
Suppressor:	ASRS 300 4mm
setting:	149mA
Detector:	Thermo conductivity detector
Flow rate:	1.200ml/min
Mobile Phase:	50mM sodium hydroxide (NaOH)
Gradient:	Isocratic
Injection Loop Volume:	25ul

10.13.2.2.2.6 Cation – System 3 – Suggested Parameters:

Note: Standard mixture for System 3: lithium, sodium, ammonium, potassium, magnesium, calcium

COLUMNS:

Column:	Dionex IonPac CS12A 4 x 250mm
Guard column:	Dionex IonPac CG12A 4 x 50mm
Suppressor:	CSRS 300 4mm
setting:	59mA
Detector:	Thermo conductivity detector with Thermo DS6 heated conductivity cell
Flow rate:	1.000ml/min
Mobile Phase:	20mM methanesulfonic acid (CH_3SO_3H)
Gradient:	Isocratic
Injection Loop Volume:	25ul

10.13.2.2.2.7 Procedure for Analysis

Anion analysis:

Prepare samples from items for which anion analysis is desired, and H2O blanks using 18.2 MΩ deionized/purified H2O and IC sample vials. Transfer a sample of the Anion standard mixture sample to an IC sample vial. 0.5 ml or 5 ml sample vials can be used for all samples.

Load all vials into the autosampler associated with the ICS 5000 instrument. Create a sequence in the software in Systems 1/2 (folder LS-TR-IC-1) to include Anion Standard mix, H2O blanks and case items, inserting a blank before each case item. Start sequence and wait until complete.

When a run is complete, gather data from the two columns/channels/Systems associated with the ICS 5000 (see 2.5.4.4 and 2.5.4.5). Print data as .pdf files onto a removable disk, for inclusion into the case file record.

Cation analysis:

Prepare samples for which cation analysis is desired, as above, using the same 18.2 MΩ deionized/purified H2O for case items and H2O blanks, and prepare an IC vial with the Cation Standard mixture.

Load all vials into the autosampler associated with the ICS 1100 instrument. Create a sequence in the same manner as above, but in System 3 (folder LS-TR-IC-2), and start the sequence.

When runs are complete, obtain data from System 3 (see 2.5.4.6). Print data as a .pdf file onto a removable disk, for inclusion into the case record.

10.13.2.2.2.8 Identifications

Identifications are made by comparison of retention times with known standards from the Anion and Cation Standard mixtures.

10.13.2.2.2.9 References

Doyle, J. M. and McCord, B. R. Novel electrolyte for the Analysis of Cations in Low Explosive Residue by Capillary Electrophoresis, Journal of Chromatography B (1998) 714:105–111

Doyle, J. M., Miller, M. L., McCord, B. R., McCollam, D. A., and Mushrush, G. W. A Multicomponent Mobile Phase for Ion Chromatography Applied to the Separation of Anions from the Residue of Low Explosives, Analytical Chemistry (2000) 72:2302–2307

Miller, M.L., Doyle, J.M., Lee, R.A., Gillette, R. Analysis of Anion by Capillary Electrophoresis and Ion Chromatography for Forensic Applications; For. Sci. Comm. April 2001, Vol. 3 Number 2

10.13.2.2.3 Scanning Electron Microscope – Energy Dispersive X-Ray (SEM-EDS)

10.2.2.2.3.1 Introduction

The Scanning Electron Microscope/Energy Dispersive X-Ray Spectrometer (SEM-EDS) analysis alone is not sufficient for identification of chemical reagent identification. SEM-EDS is used to obtain the elemental composition of a sample. The SEM can also be used to obtain a secondary electron image of a sample, or a backscattered electron image of a sample.

10.13.2.2.3.2 Safety Considerations

The x-ray detector uses liquid nitrogen. Care must be used to protect the eyes and skin while working with liquid nitrogen.

10.13.2.2.3.3 Preparations

Sample stubs for SEM.

Carbon tape for mounting samples on SEM stubs.

Copper and aluminum for calibration.

10.13.2.2.3.4 Instrumentation

Scanning Electron Microscope – with attached Energy Dispersive X-ray Spectrometer.

10.13.2.2.3.5 Procedure or Analysis

Mount sample on carbon tape. Mount copper metal on an aluminum stub.

Calibrate the x-ray EDS with copper and aluminum.

Calibrate and run samples at 25 kV acceleration voltage. Save calibration on hard drive.

Print or save calibration spectrum for inclusion with sample spectra.

Mount and analyze the case sample.

Label and save/print each EDS spectra with the associated secondary electron image, for inclusion in the case file.

10.13.2.2.3.6 Minimum Standards and Controls

Perform appropriate instrument function verification(s).

10.13.2.2.3.7 References

Glattstein, B.; Landau, E.; Zeichner, A. "Identification of Match Head Residues in Post-Explosion Debris"; Journal of Forensic Sciences, 1991, 36, 5, 1360-1367.

Flegler S, Heckman, J, Klomparens K, Scanning and Transmission Electron Microscopy : An Introduction , 1993, ISBN: 0195107519

10.13.2.2.4 Micro- X-Ray Fluorescence (u-XRF)

10.13.2.2.4.1 Introduction

u-XRF analysis alone is not sufficient for identification of chemical reagent identification. Identification requires at least one additional supporting technique.

10.13.2.2.4.2 Safety Considerations

See FSD Safety Manual.

10.13.2.2.4.3 Instrument Calibration & Verification

The u-XRF must be calibrated each day it is used for casework analysis. Using the calibration function within the instrument's software and a calibration standard (typically aluminum and copper). Calibrate the instrument at each Time Constant that will be used. The calibration data is automatically stored by the software.

Collect instrument verification data each day of instrument use.

10.13.2.2.4.4 Sample Preparation

The samples should be mounted using materials that contribute negligible elemental content, such as Kapton film stretched over an opening of a mounting apparatus.

10.13.2.2.4.5 Recommended parameters

At least 3 collection points from each sample (known and question) from different locations on each sample; minimum of 200 LSec; 50 kV; adjust power (uA) to the maximum power that produces <50% Dead Time.

10.13.2.2.4.6 Spectral Comparison

Spectral comparison consists of comparing the elements present in the known samples to the elements present in the questioned samples.

10.13.2.2.4.7 Multi-runs - Different Days

If quantitative or semi-quantitative statistics will be evaluated, a reference sample should be analyzed at the beginning and end of each multi-point run to verify the stability of the instrument throughout the run and to allow for inter-day comparison of data. To allow for comparison of data from different days, reference sample spectra for those days should be indistinguishable (spectral comparison method) and the parameters should be similar. This sample may be NIST SRM 1831 and can function as the instrument verification check. (See Instrument Standards and Controls for X-Ray Fluorescence)

10.13.2.2.4.8 References

Fischer, R. and Hellmiss, G. Principles and Forensic Applications of X-ray Diffraction and X-ray Fluorescence. In: Advances in Forensic Sciences. Volume 2, H. C. Lee and R. E. Gaensslen, eds. Year Book Medical Publishers, Inc., Chicago, 1989