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Two Sampling Methods to Enhance the Safety Professional's Air Monitoring Capabilities

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Introduction

Have you ever had a telephone call that starts out like this: "Hi, I have an unknown odor in my building and I would like you to tell me what it is?" Or: "Hi, I have a mixture of about 20 different Volatile Organic Compounds (VOCs), ranging from alcohols to xylenes. I have a limited budget, so can you collect them all at the same time on one sample?" If you did, what was your initial reaction? If you are like many Heath and Safety Professionals, it was probably to cringe. You knew you were going to have a hard time explaining to your potential client, either external or internal, that there is no magic black box that can tell you what is causing that odor or that will allow you to collect all those VOCs at once. Although there is still no magic black box, in recent years, two methods have been developed and refined that can make those types of phone calls much more enjoyable for everyone involved.

Overview of Methodology

These 2 methods are very different from one another and have been developed in direct response to the type of telephone calls mentioned above. Both methods are suitable for known or unknown VOCs. One is a modification of a traditional OSHA method, OSHA Method 7. The other method has been modified from an EPA ambient air method and is now called OSHA PV2120.

Sample collection follows the traditional OSHA 7 method. Samples are collected using personal sampling pumps calibrated at 0.2 liters per minute on a standard charcoal tube. The modification takes place in the laboratory, during the desorption of the charcoal tube. In place of the traditional carbon disulfide extraction solvent, co-solvents, sometimes called universal solvents, are used to amplify the carbon disulfide extract prior to GC/FID analysis. The make up of the universal extraction fluid varies from laboratory to laboratory and is usually not made public. They are made of various polar and non-polar solvents of differing concentrations. The laboratory must have all of the required method QC in place before this modification is used. This includes desorption efficiencies, curve linearity, and detection limits. In addition to active sample collection with pumps and tubes, universal solvent extraction can also be applied to passive organic monitors. Once the samples have been desorped, the rest of the analysis follows the standard OSHA 7 procedures. The extracts are injected into a GC equipped with a FID detector.

Not all laboratories have developed universal solvents. Those that have will have different lists of reported VOC's.

OSHA has now modified EPA TO 15, which made use of 6 liter Summa Canisters for ambient air collection, for personal air sampling. OSHA Method PV 2120 uses mini evacuated canisters followed by GCMS analysis. Either 440 cc or 1 liter of air can be collected depending on the size of the canisters used. The sample can be collected instantly or the canister can be fitted with a regulator to collect an integrated air sample over any time period up to 24 hours. A maximum of 63 VOCs can be quantified down to the PPB range. The major differences between EPA TO15 and OSHA PV2120 are the size of the canisters and the maximum length of sampling time. EPA TO 15 uses 6 liter canisters and can sample for several days continuously. OSHA PV 2120 uses either 440cc or 1 liter canisters and can collect a sample for to 24 hours (when using the 1liter cans). In addition to the quantification of the standard 63 VOCs, a request for a library search on unknown compounds can be made. The GCMS instrument has a library of over 75,000 mass spectra that correspond to known compounds. The unknown spectra are compared to the library data to produce Tentatively Identified Compounds (TICs). Since the GCMS is not calibrated for these compounds, only an estimated concentration can be reported. This library search is similar to fingerprint identification and is useful in identifying unknown VOCs that are present.

The Differences Between GC/FID and GCMS Instrumentation

With GC/FID analysis, a portion of the sample extract is injected into the GC instrument. It is volatilized by heat and swept through a column containing various resins. The individual VOCs become separated in the column and pass by the FID, where they are detected and converted to electrical signals. The signals are then identified as individual peaks by the recorder. See Figure 1. The amount of time that it takes a specific compound to pass through the column and into the FID is called the retention time. All VOC identification is performed by comparing the retention times of known standards to the retention times of the VOCs detected in the sample.

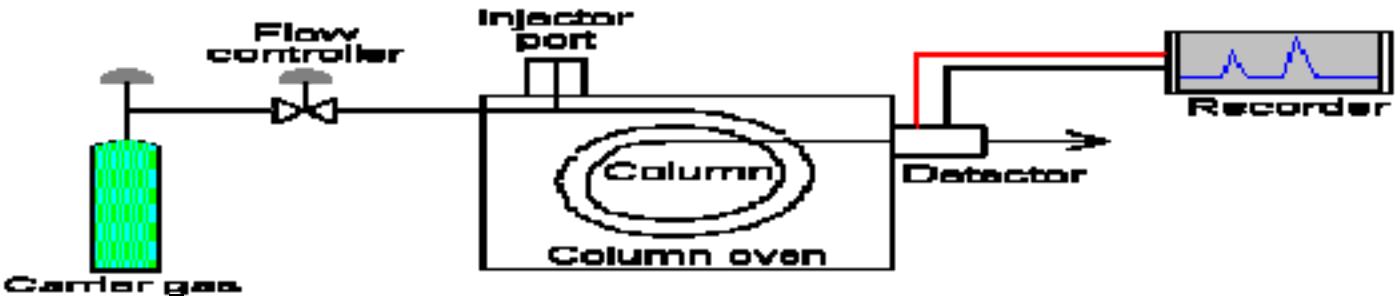

Figure 1

GCMS instruments use with the same principals of GC instrument but go a step further. In place of the desorption solvent being injected into the GC, a sample of the whole air is injected into the GCMS. As in the GC analysis, the sample is volatilized by heat and swept through a column containing various resins. When the individual VOCs become separated they pass into the MS

portion of the instrument. The compounds are then bombarded by electrons from the ionization source of the mass spec. This bombardment produces a unique fingerprint or mass spectral pattern that will pass through an ion analyzer. See Figure 2. The compounds are first identified by their individual retention times and then confirmed by comparing their mass spectra with the mass spectra of the known standard. If the mass spectra does not match the standard, the compound becomes an unknown and can be compared against the mass spectra library to become a TIC as previously described.

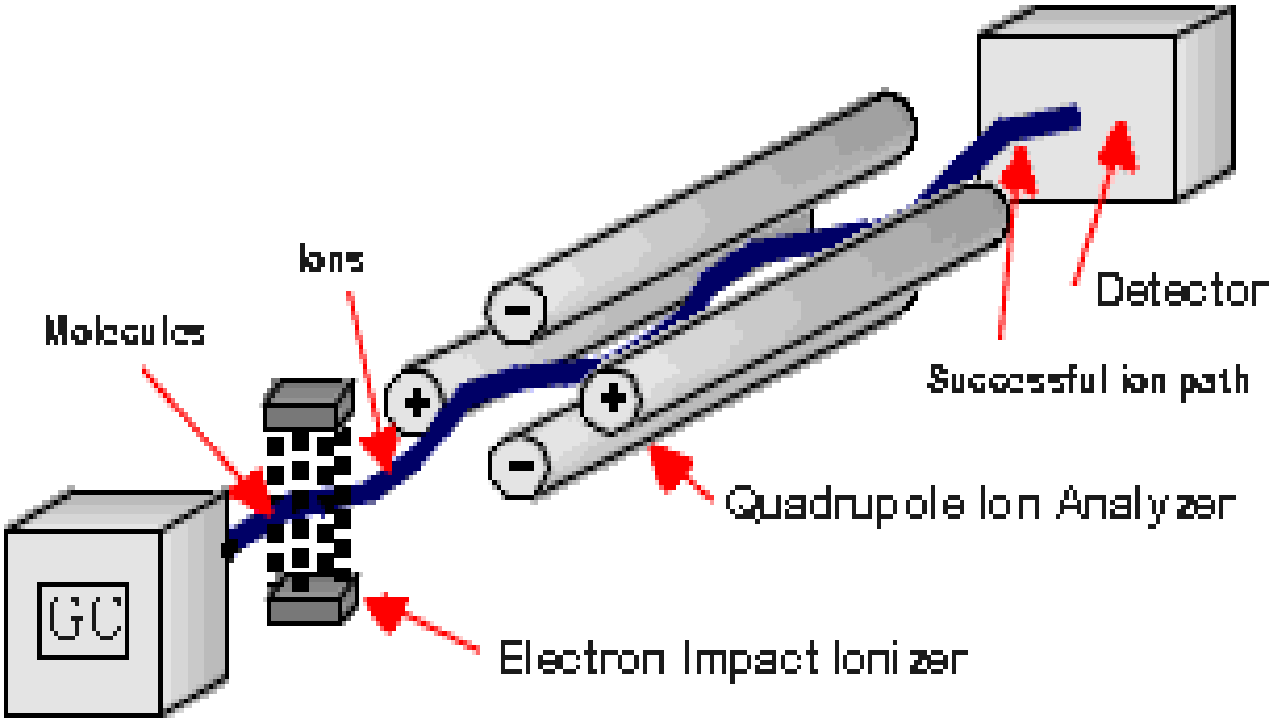

Figure 2

When to Use Modified OSHA 7

Since there is no difference in the field collection portion of modified OSHA 7, it can be used anytime that OSHA 7 would normally be used. In addition to being able to collect and analyze for aromatic and aliphatic hydrocarbons, alcohols, ketones, and cellosolves can also be collected and analyzed on the same tube. This saves time in money in sample collection and laboratory analysis. Depending upon the laboratories standard list, over 100 VOCs could be sampled for at the same time. An example of such a list is presented in Table 1.

Guidelines for when to use OSHA 7 /modified OSHA 7:

- **Concentrations higher then 1 PPM**
- **Spills, confined spaces, head spaces**
- **Mixtures such as gasoline and other fuels**
- **Personal sample exposures – both STEL and 8 hour TWA**
- **Area samples**

1,1,2-Trichloroethane	Cyclohexane	Methyl Cellosolve
1,1-Dichloroethane	Cyclohexanone	Methyl Cellosolve Acetate
1,1-Dichloroethylene	Cyclohexene	Methyl Chloroform
1,2-Dichloroethane	Diacetone Alcohol	Methyl Ethyl Ketone
1,1,2,2-Tetrachloroethane	m-Dichlorobenzene	Methyl Isobutyl Ketone
1,2,4-Trimethylbenzene	o-Dichlorobenzene	Methyl Propyl Ketone
1,2,3-Trimethylbenzene	p-Dichlorobenzene	Methylene Chloride
1,3,5-Trimethylbenzene	1,2-Dichloroethylene	Naphthalene
3-Methyl Styrene	cis-1,2-Dichloroethylene	Octane
4-Methyl Styrene	trans-1,2-Dichloroethylene	Pentane
Acrylonitrile	DIETGMEE	PGMMEE
Aromatic 100	DIETGMMEEACT	PGMMEEACT
Aromatic 150	Dioxane	4-Phenylcyclohexene
Amyl Acetate	DPGMMEE	Phenyl Glycidyl Ether
Acetone	Epichlorohydrin	n-Propyl Acetate
Benzene	Ethanol	n-Propyl Alcohol
Benzyl Alcohol	Ethyl Acetate	Stoddard Solvent
n-Butanol	Ethyl Acrylate	Styrene
sec-Butanol	Ethyl Benzene	Tetrachloroethylene
n-Butyl Acetate	Heptane	Tetrahydrofuran
Butyl Cellsolve	n-Hexane	Toluene
Butyl Cellsolve Acetate	Isobutyl Acetate	Trichloroethylene
Butyl Chloride	Isopar G	Turpentine
Butyl Glycidyl Ether	Isopropyl Acetate	Vinyl Chloride
Carbon Tetrachloride	Isohexene	Vinyl Toluene
Cellosolve	Isobutanol	m-Xylene, p-Xylene
Cellosolve Acetate	Isopropanol	o-Xylene
Chlorobenzene	Kerosene	p-Xylene
Chloroform	Methyl Alcohol	Xylenes
Cumene	Methyl Amyl Ketone	VM&P

Table 1

Limitations of OSHA 7 /modified OSHA 7:

The limitations associated with modified OSHA 7 are the same as OSHA 7. It should not be used if it is suspected that very low (sub ppb) levels of contaminates are present. It will not sample for dust or particulate, VOCs that will not adsorb onto charcoal, or Non-VOC compounds such as inorganic acids. The method should not be used if it is required to sample for longer then 8 hours or if an instant (grab) sample is required.

When to Use OSHA PV2120

OSHA PV2021 can be used in many situations where traditional sampling will not work. Concentrations of VOC's can be detected in the PPB range, analytes present for a very short period of time can be captured, unknown VOC's present can be identified as TICs and estimated concentration can be reported, or extended sampling periods can be acuminated. In addition to the 63 compounds that can be quantified (see Table 2), you can get estimations of unknown VOC concentrations**.**

Guidelines for when to use OSHA PV2120:

- **Very low concentrations, PPB range**
- **Analytes present for very short period of time**
- **Unknown VOCs present**
- **Sampling up to 24 hours**
- **Personal sample**
- **Area samples**
- **Product offgassing**
- **IAQ studies**

Acetone		1,1-Dichloroethene		Methy Ethyl ketone (MEK)
Allyl chloride		cis-1,2-Dichloroethene		Methyl Isobutyl ketone (MIBK)
Benzene		trans-I,2-Dichloroethene		Methyl t-butyl ether (MTBE)
Benzyl Chloride		1,2-Dichloropropane		Propylene
Bromodichloromethane		cis-1,3-Dichloropropene		Styrene
Bromoform		trans-1,3-Dichloropropene		1,1,2,2-Tetrachloroethane
Bromomethane		1,4-Dioxane		Tetrachloroethene
1 ,3-Butadiene		Ethyl Acetate		Tetrahydrofuran
Carbon disulfide		Ethyl chloride (Chloroethane)		Toluene
Carbon Tetrachloride		Ethylbenzene		1,2,4-Trichlorobenzene
Chlorobenzene		4-Ethyltoluene		1,1,1-Trichloroethane
Chloroform		Freon 11		1,1,2-Trichloroethane
Cyclohexane		Freon 12		Trichloroethene
Chloromethane		Freon 113		1,2,4-Trimethylbenzene

Dibromochloromethane		Freon 114		1,3,5-Trimethylbenzene
I ,2-Dibromoethane		Heptane		2,2,4-Trimethylpentane
o-Dichlorobenzene (1,2-)		Hexane		Vinyl acetate
m-Dichlorobenzene (1,3-)		Hexachloro-1,3-butadiene		Vinyl bromide
p-Dichlorobenzene (1,4-)		Isopropyl alcohol		Vinyl chloride
1,1-Dichloroethane		Methylene chloride		o-Xylene
1,2-Dichloroethane		Methyl Butyl ketone		m,p-Xylene

Table 2

Limitations of OSHA PV2021

As with all sampling methods for vapors, OSHA PV2021 should not be used when trying to sample for dust or particulate. Due to the sensitivity of the method, it should not be used for total hydrocarbons, chemical spills, or stationary source samples. Semi-volatile compounds, polymers, mercaptans or other sulfur compounds, and compounds with molecular weight of less then 35 cannot be collected by this method.

Conclusion

Although there is still no magic black box available for those pesky telephone calls we all get from time to time, we are getting closer. No longer do you have to tell your client that it will take weeks and thousands of dollars to give them what they are asking for. Now in less then a week and a few hundred dollars, you can provide the client with information about what is in the air or even just as important, what is not in the air. Each of the methods described have their place in the field of health and safety monitoring. Your laboratory can assist you in deciding which of these methods would be appropriate for your situation. So next time the telephone rings, and the person on the other end starts the conversation with “I have this funny odor…” you do not have to cringe.

Bibliography

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