Specialty Gas Analysis Using Atomic Emission Detection

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In the semiconductor industry, increasing chip performance has led to an increasing demand on gas manufacturers to raise the quality of their precursor gas products. This demand has resulted in the need to measure impurities real or imagined at lower and lower levels. In the area of gas chromatography this means using more sensitive, specific, and smarter detectors. Gas chromatography/mass spectrometry (GC/MS) has long been one of the choices for fulfilling such a role. In recent years gas chromatography coupled with atomic emission detection (AED) has become as powerful a tool quantitatively as GC/MS is qualitatively.

AED has a number of appealing analytical attributes: it can measure with reasonable specificity most elements; it is reasonably linear; it is sensitive for most elements of interest in the electronic and specialty gas industry; and perhaps most importantly, its atomic specificity is independent of the molecule. These attributes combined, make the AED at least as powerful as mass spectrometry on many unknown impurities in gas samples. This article will discuss all of these attributes, some of which are based on real world problem solving.

Detection Limits and Linearity

Available in the instrument "recipes" are estimates of detection limits appropriately described in units of picograms per second. For example, carbon detection is 0.5 pg/sec, sulfur is 1 pg/sec, and iron is 0.05 pg/sec. While these guidelines are useful they do not convey the detection limit that might be accomplished in the course of a typical analysis based on what a customer would find useful for product specification. More appropriately, the detection limit for carbon monoxide in NF_3 would be 5 ppb. The detection limit for silane in bulk phosphine would typically be 2 ppb. And the detection limit for iron carbonyl in hydrogen or syngas would be about 0.5 ppb. These are values that take into consideration the chromatographic system and our ability to offer the system a low level stable standard. Figure 1 describes a series of injections of a silane standard at the 5 ppb level. Consideration is given here to the chromatographic system and our ability to offer the system a low level unreacted standard.

It is worth noting that this detection limit is a 20 to 50 times greater detection level than what can be achieved using a flame ionization detector. A plot of the silane standard over the range of 5 ppb to 50 ppm is described in Figure 2. This indicates linearity over 4 orders of magnitude.

This would be typical of most elements. Silane was chosen in this study because we were interested in determining its stability on wetted surfaces at low concentrations.

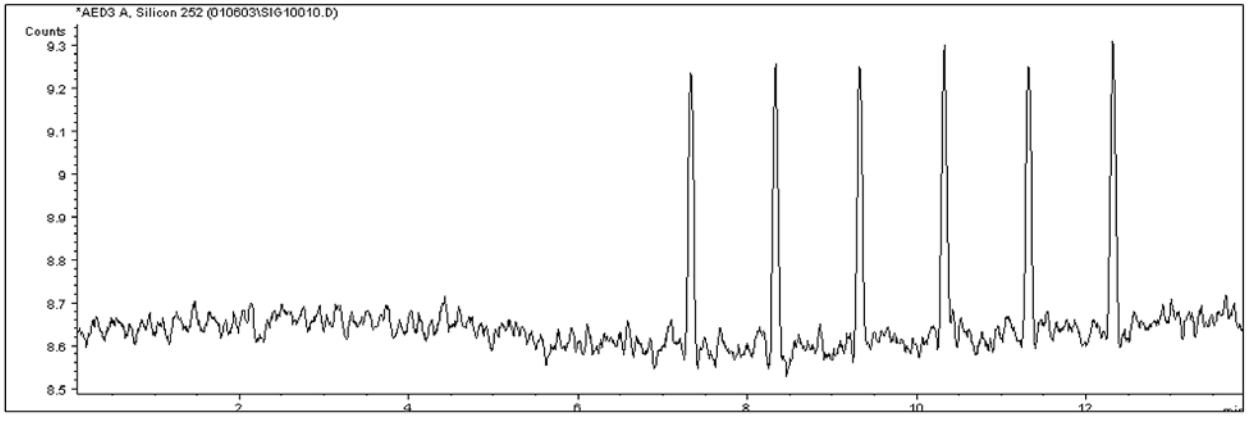

Figure 1: 5 ppb Silane

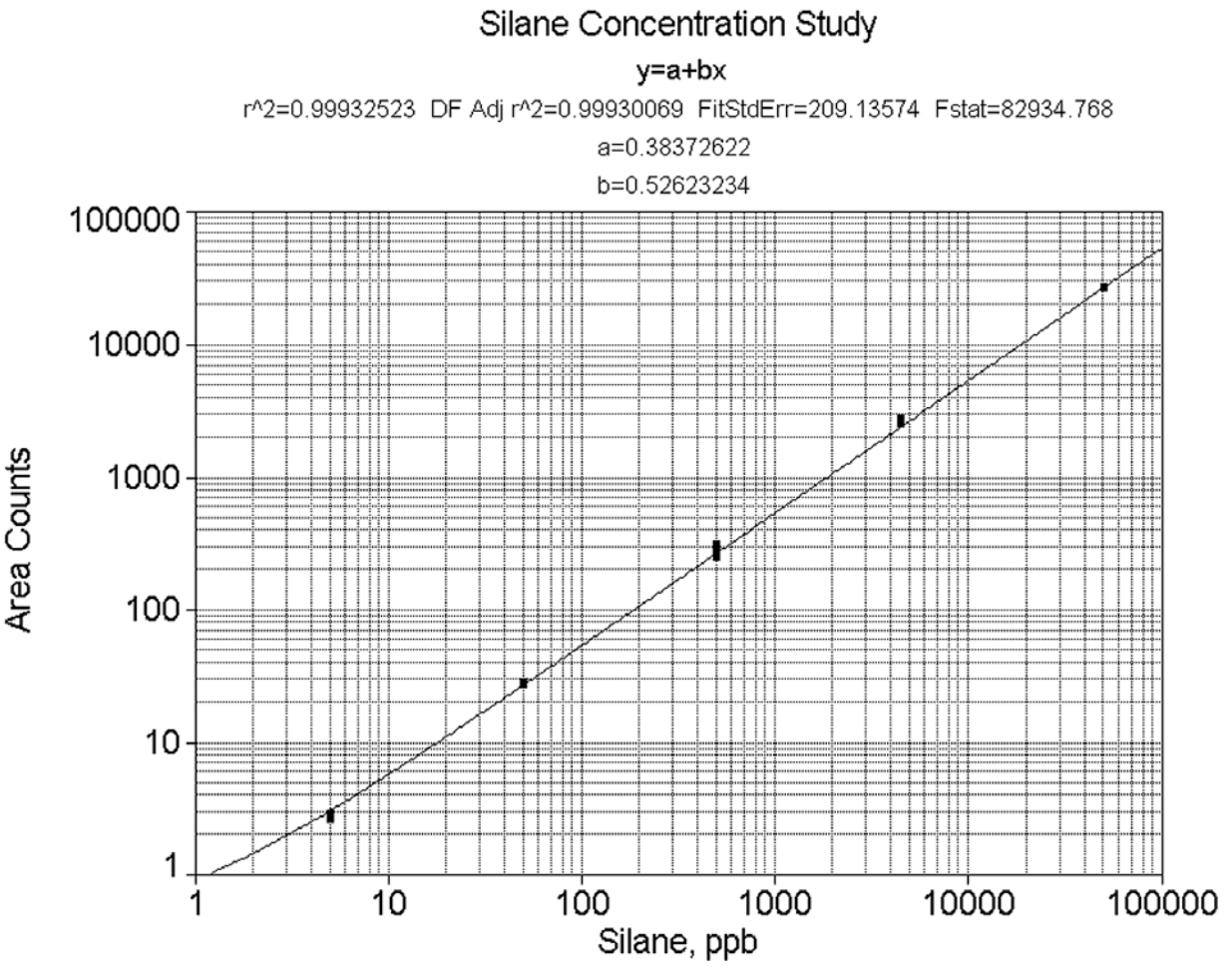

Figure 2: Silane linearity

Challenging One's Standards

Carbon Compounds

One of the standards frequently used in our laboratory is a multi-component mix composed of a number of "fixed gases" including carbon monoxide, methane, and carbon dioxide. This is usually purchased at a nominal concentration of 2 ppm. Figure 3 and Table 1 describe the results of analyses of three different standards.

Since the AED provides absolute atomic response, all three components should have had the same response per atom. Agilent calls this attribute Compound Independent Calibration, although we think of it as element or atom specific detection. We knew bottle A was reasonably accurate based on comparison with a different 100 ppm standard mix. The CO was a little low as one might expect due to its slightly 'sticky' performance with the column materials. However, it was obvious that bottle C was a mess, probably due to serious contamination with lab air at low pressure. Our experience in qualifying standards at this level is that the gravimetric blend data is usually much more accurate than the certification value. This is because the vendor, although using NIST traceable standards, has no real consistent methodology because they are often using three separate standards on two or more instruments. For gravimetric mixing they are usually only using one balance.

Silane Homologs

Contaminants of interest in silane include methyl silane, disilane, and ethylsilane. The typical problem with these standards are that most gas vendors use an FID to certify their blends. In addition, disilane is very unstable. In this case we qualified a mixture of methylsilane and disilane against a previously qualified standard of 75 ppm silane. Our findings are illustrated in Figure 4 and table 2. This data demonstrates that the reported disilane value is indeed somewhat lower than its certification value.

Transitional Standardization

Metal Hydrides

The previous example begs the question 'how was the silane verified in the first place?' The silane as well as

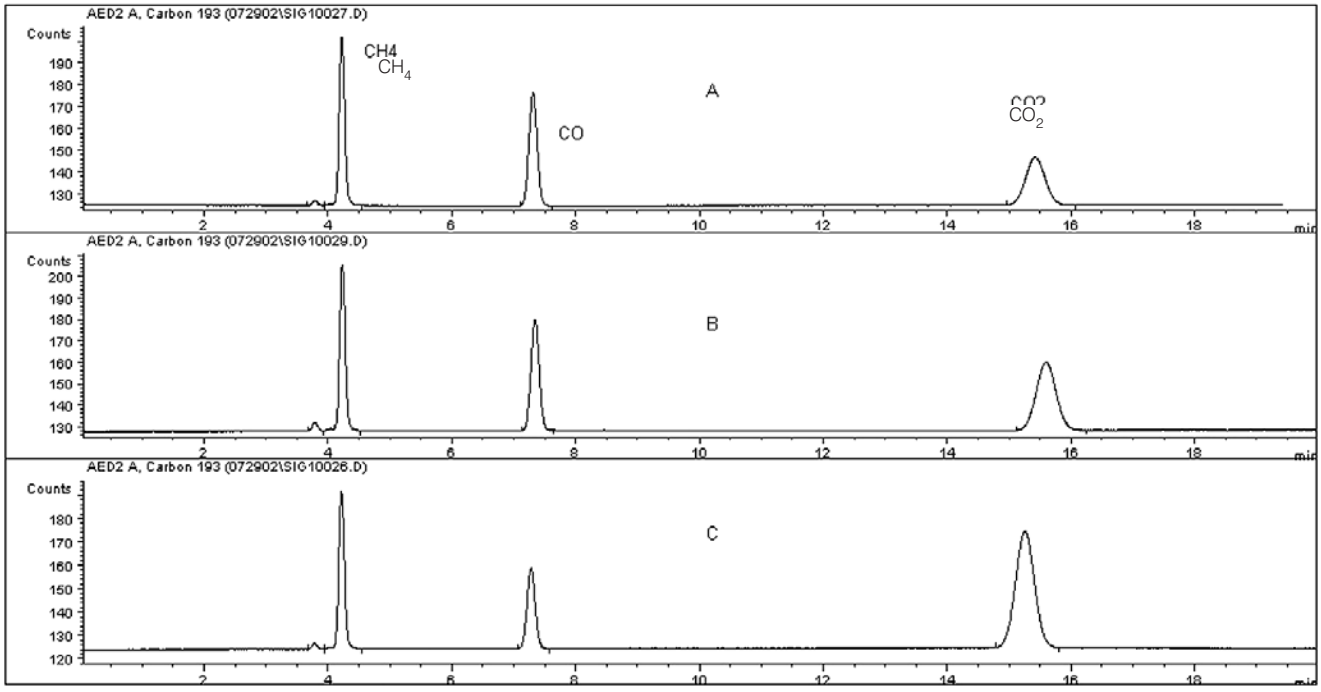

Figure 3: Analyses of three different standards

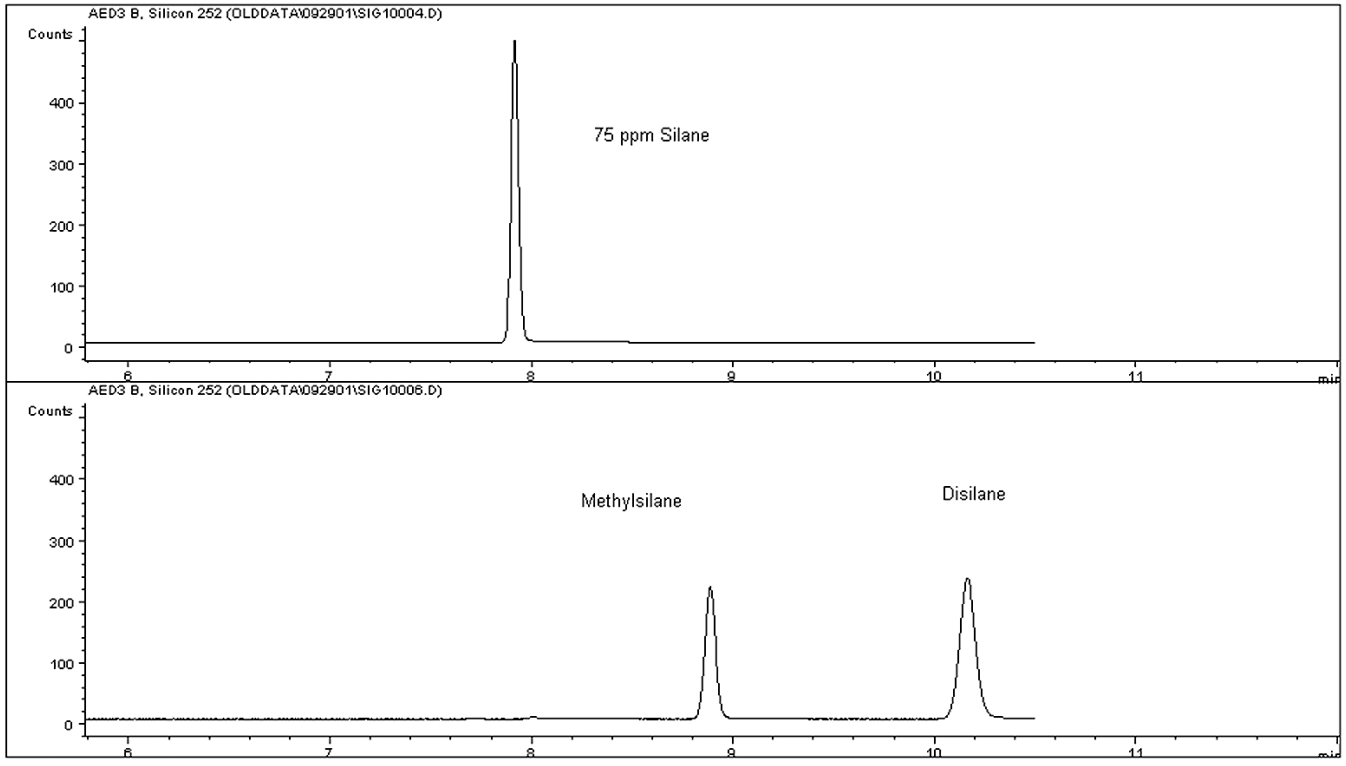

Figure 4: Mixture of methylsilane and disilane against a previously qualified standard.

	CO	CH_4	CO_2
Cylinder	Area counts per atom ppm		
A	219	254	240
B	210	231	256
C	379	289	892

Table 1: Results of analyses of three different standards

Area counts per Si atom ppm	Area counts per Si atom ppm	Vendor Certification ppm	Found Concentration ppm
Silane	16.7	---------	---------
Methylsilane	16.3	50	48.8
Disilane	12.6	50	37.7

Table 2

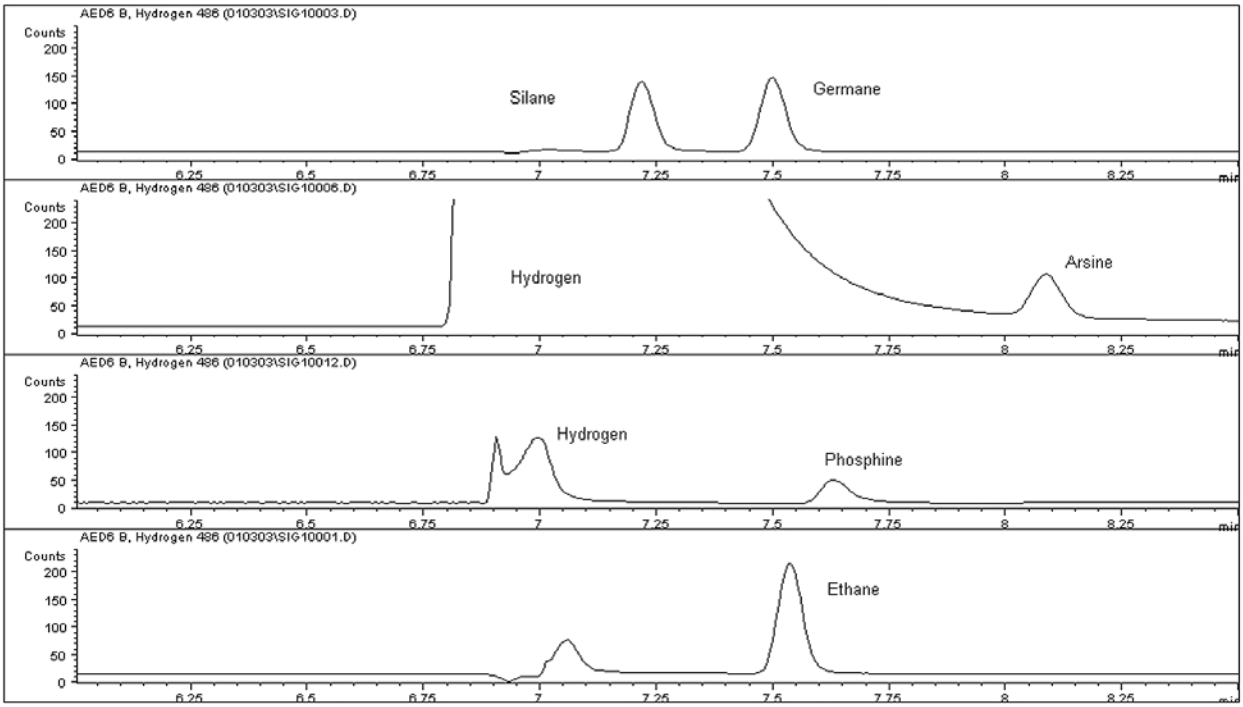

Figure 5: Results of several metal hydride standards against an ethane standard containing other hydrocarbons.

	Area Counts Hydrogen Signal	No. H_2 Atoms per Molecule	Area Counts per Atom	Declared Conc. ppm	Found Conc. Ppm
Ethane	758	6	126.3	100	100
Butane	1258	10	125.8	100	99.6
Pentane	1506	12	125.5	100	99.3
Arsine	340	3	113.3	100	89.7
Silane	456	4	114	100	90.2
Germane	515	4	128.8	100	101.9
Phosphine	199	3	66.3	100	52.5

Table 3

	Calculation of Metal Carbonyl based on Carbon mol Response				
	Hexane			**Iron Carbonyl**	
	Standard Concentration	80	ppb mol		
	Area Counts (C 193 nm)	25		Area Counts (C 193 nm)	52
	Carbon Moles	6		Carbon Moles	5
	Concentration = Sx Area Cts. X Std. Conc. X Std # moles / Std. Area Cts. X Sx # moles				
i.e.	Concentration = 52 x 80 x 6 / 25 x 5 = 200 ppb mol $Fe(CO)_5$				

Table 4: Calculation of Metal Carbonyl based on Carbon mol Response

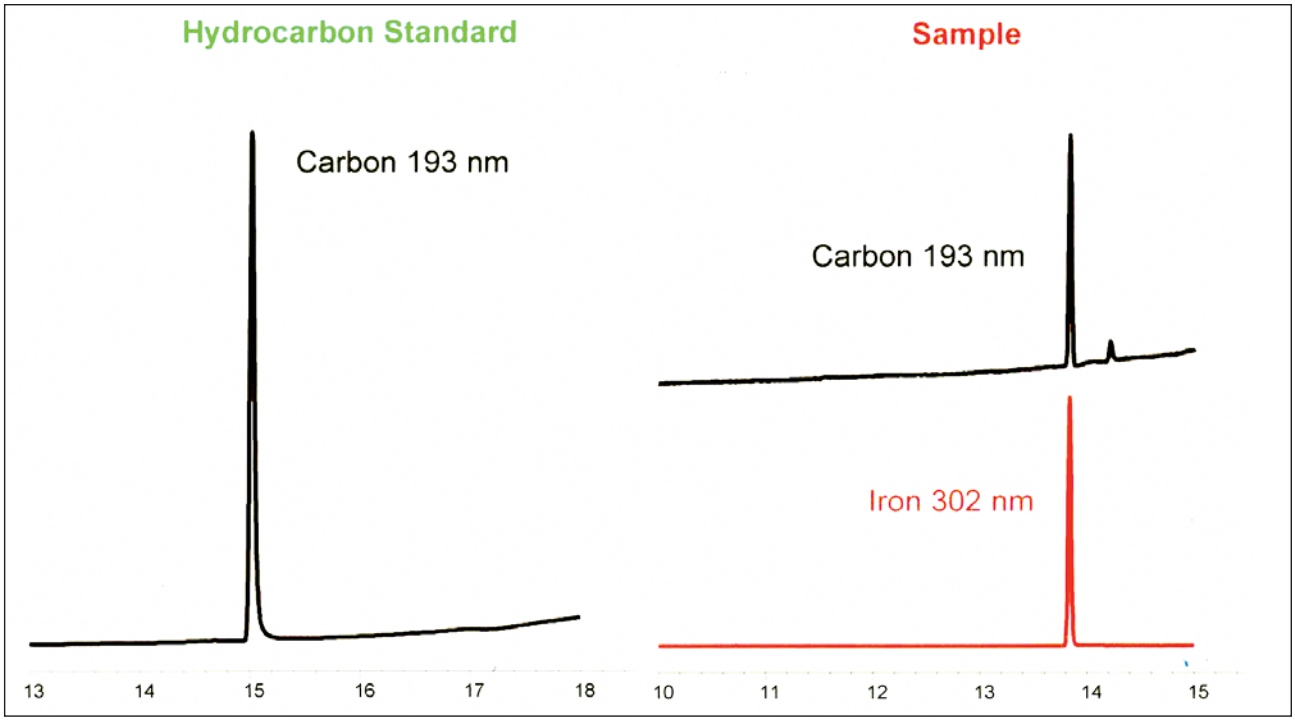

Figure 6

other exotic standards can be verified against a standard that is more readily attainable, stable and easier to verify by conventional means. We can use a hydrocarbon standard to verify metal hydride standards by measuring the hydrogen content.

Figure 5 and Table 3 illustrate the results of several metal hydride standards against an ethane standard containing other hydrocarbons. A hydrogen "recipe" was used for quantitation. The arsine standard was in a cylinder of hydrogen balance gas. The hydrogen seen in the phosphine standard may be a result some decomposition which would explain its low recovery of 52.5 ppm.

Metal Carbonyls

Nickel and iron carbonyl are considered problematic in many processes. Due to their toxicity and labile nature, standards are virtually non-existent. Both can be generated in the laboratory. The electron capture detector has very good sensitivity for both, but is a difficult detector to work with and still poses the problem of calibration. You guessed it! The calibration can be made by

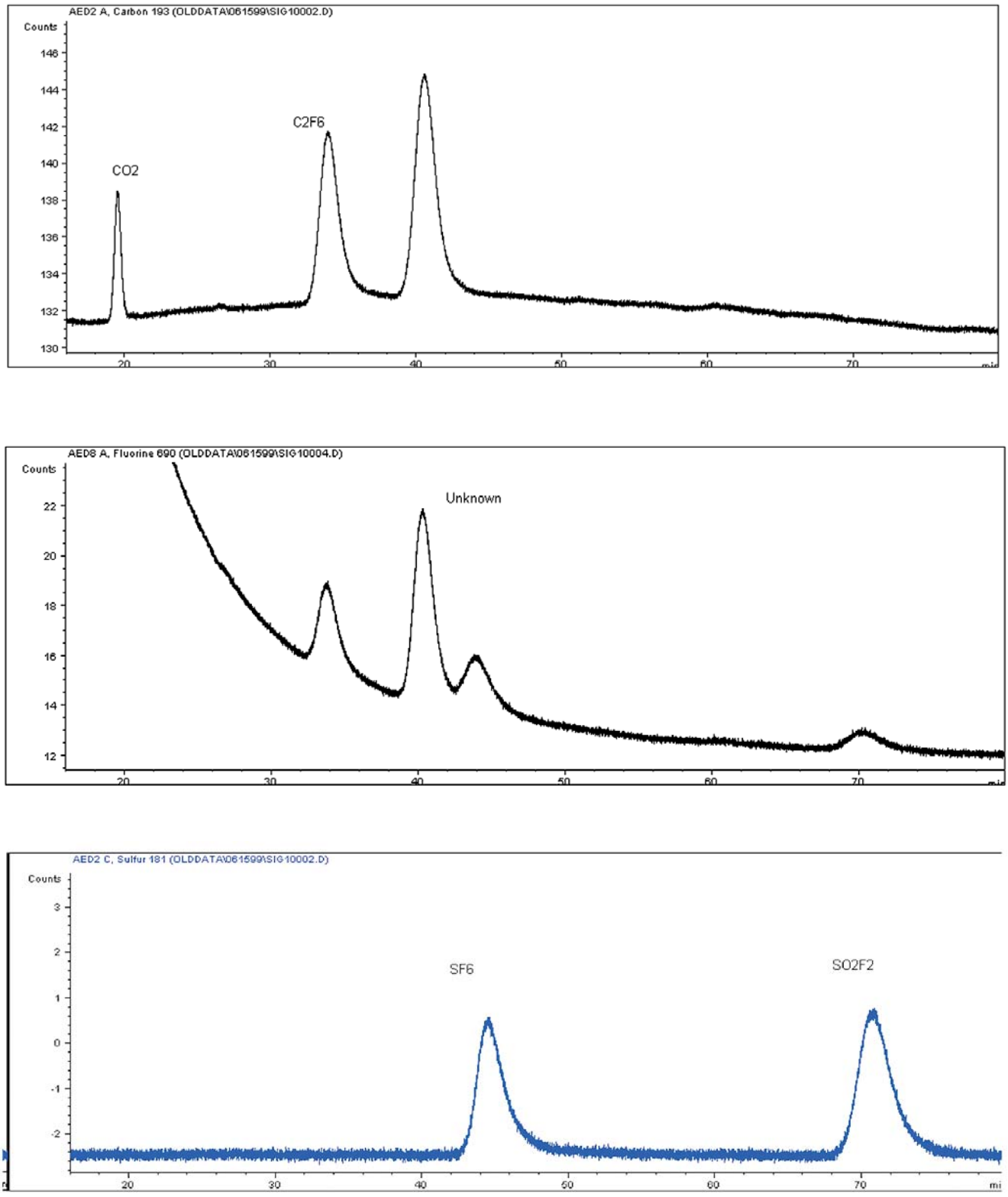

Figure 7: Chromatograms of carbon, fluorine and sulfur.

running the sample against a carbon based standard as illustrated below in Table 4.

Once this is accomplished the sample can be re-run using the iron recipe. At this point an iron sample of much lower concentration can be analyzed at levels well below carbon detection limits. A graphical representation of this strategy is described in Figure 6.

Compound Identification (Sleuthing)

In our laboratory, nitrogen fluoride is routinely analyzed by GC using a pulsed discharge detector. Normally about 11 impurities are measured chromatographically. Occasionally, an unidentified compound would appear in the analysis. Eventually this unidentified component became of some concern to the customer. Initially, mass spectrometry was used for identification. Using electron impact ionization, the largest ion found was m/z 69 with traces of m/z 50 and m/z 31. These are typical ions for fluorinated hydrocarbons and represent the CF_3+ ion. The pattern was a perfect match with carbon tetrafluoride.

Since CF_4 was already identified and accounted for, it was obvious that more information than mass spectral data was needed. GC-AED was employed using carbon, fluorine and sulfur recipes. Chromatograms of these elements are illustrated in Figure 7. The fluorine to carbon area ratio for perfluoroethane was 0.397 representing a 3:1 atom ratio. The fluorine to carbon area ratio for the unknown was 0.580 making the atom ratio about 4.4:1. At first this didn't make sense since the only fluorocarbon with a higher ratio than 3:1 would be CF_4 (again already accounted for). This prompted us to re-run the sample using the nitrogen recipe. A small peak was found at the retention time of the unknown. Assuming the 4.4:1 ratio had some error in it and that it might actually be 5:1 it was hypothesized that the molecule was perfluoromethylamine (NF_2CF_3). This made sense as an impurity existing as methylamine in the NF_3 precursor material ammonia. In order to prove this hypothesis, the sample was re-analyzed using GC/MS, and this time methane chemical ionization was employed. Methane chemical ionization is a 'softer' ionization process that typically adds a proton to the molecular weight of the bombarded species. In this case we obtained spectra with the only significant ion being m/z 122.

Subtracting the one proton meant that the molecular weight of our unknown was 121. This was conclusive proof that our unknown was perfluoromethylamine — to wit:

Perfluoromethylamine = NF_2CF_3

1 N = 14

5 F = 5 x 19 = 95

1 C = 12

Total = 14 + 95 + 12 = 121.

Conclusion

- GC–AED is a rapid, simple, direct, and species specific analytical procedure with ppb level detection limits.
- The ability to detect carbon and or hydrogen in compounds as well as other elements allows for very inexpensive standardization. It is unnecessary to rely on standards that may decompose quickly or become unstable vs. the stability of carbon / hydrogen in a hydrocarbon gas standard.
- Element specific
- Linear
- Equi-atomic response to compounds makes standardization much more efficient than GC-ECD and GC/MS.

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