What sets the Mass Spectrometer apart from other forms of detectors is the ability to selectively-identify individual masses. Figure 5 shows the Total Ion Chromatogram (TIC) of a mixture of 100 ng/µL Toxaphene and 0.10 ng/µL Pesticide Mix. The Extracted Ion (EI) mass 159 is Toxaphene, and the Extracted Ion (EI) mass 66 is Aldrin which was confirmed by a NIST library search as seen in Figure 6. Aldrin is easily identified and integrated without additional preparatory procedures.

The Contract Laboratory Program (CLP) lists 0.2 ng/µL as the quantitation limit for Aroclor 1221 using an Electron Capture Detector. Figure 7 shows Aroclor 1221 well above the noise level at the 0.20 ng/µL quantitation level, using GC/MS in the SIR mode and large volume injection.

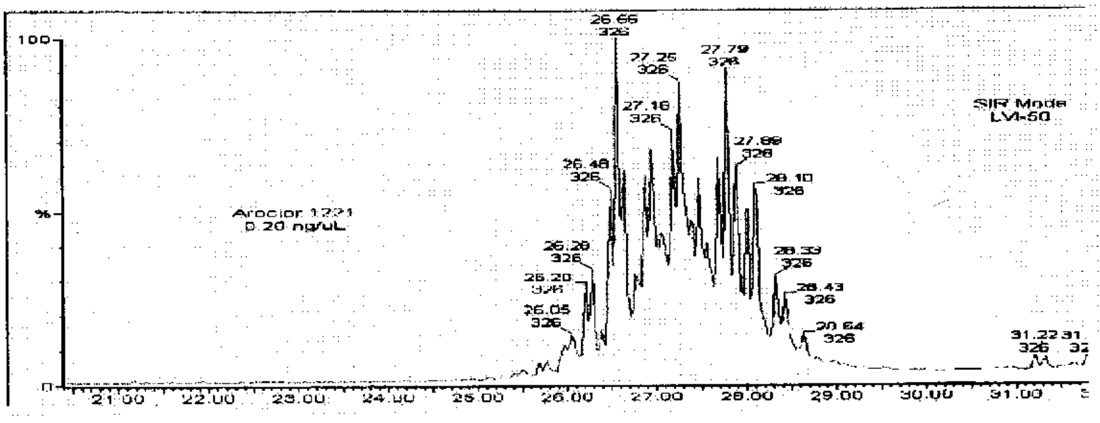

Figure 7. Quantitation Limit Pattern Recognition

SUMMARY

The ability of GC/MS to selectively identify a component based on an extracted ion chromatogram from a mixture of compounds not only assures a positive identification, but also saves time by eliminating additional cleanup and analyses. Recent technological advances in quadrupole Mass Spectrometry have increased the instrument's sensitivity. The use of Selected Ion Recording provides further sensitivity enhancements. In addition to the detector and it's mode of operation, the use of large volume injection with a programmable inlet system allow for introduction of larger sample volumes. The combination of these elements enhances the sensitivity of a GC/MS system so multicomponent analytes can be *identified and quantified* in an efficient and prOductive manner.

References

1. "Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)," in *Test Methods for Evaluating Solid Waste Physical/Chemical Methods,* SW-846, Third Edition, U.S. Government Printing Office, Springfield, VA (1996).

BENZIDINE? REALLY?

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ASI has been performing sample analysis using GC-MS Method 8270, with a variety of sample preparations from SW-846 for many years. In 1995 soil samples were received from a manufacturing site for analysis. The samples were part of a general site survey of the manufacturers facility to determine what may need remediation efforts in the future. ASI performed the requested analyses, and found and reported benzidine in several of the samples at levels approaching 1000 mg/kg. Unfortunately the data reports were simply filed by the manufacturer.

In late 1997, the manufacturing site became under consideration for sale to another company. As part of the pre-sale investigation of the site, past analytical records were examined and the benzidine results came to light. As there had never been any benzidine used or stored on the site and the manufacturing processes involved no chemical syntheses, there were some questions about the validity of the reported results.

The raw data generated during the sample analyses was examined in detail. The initial calibration was acceptable, as were the daily calibration verifications and tunes. The system performance criteria were being met. The initial calibration was used for quantitation, with retention times and user generated library spectra being updated on a daily basis. Examination of the raw chromatograms (Figure 1) from the samples revealed a hump-o-gram. Random MS scans from the hump suggested a petroleum-based background interference. Although the benzidine hits were buried in the hump-o-gram, rather than being isolated well defined peaks, the candidates matched up perfectly with the retention time and daily generated mass spectrum of the benzidine standard.

The client had not requested a library search for TIC with the original analysis. By happenstance during the data review, a library search of the questioned peak was performed. Quite surprisingly the search generated a match for dibenzothiophene, rather than the expected benzidine. Spectra of both compounds were pulled from the database for examination.

It is rather startling how similar the mass spectra of benzidine and dibenzothiophene appear in a fast visual comparison (Figures 2 and 3). Both have a dominant peak at m/z 184 and an assortment of low intensity smaller m/z signals. The two compounds have the same unit mass molecular weight (184), the only difference in the molecular formulas being the two amino groups in benzidine and the sulfur in dibenzothiophene, $C_{12}H_8(NH_2)_2$ *vs.* $C_{12}H_8S$. By coincidence the mass of the two amino groups (32) is the same as the sulfur (32).

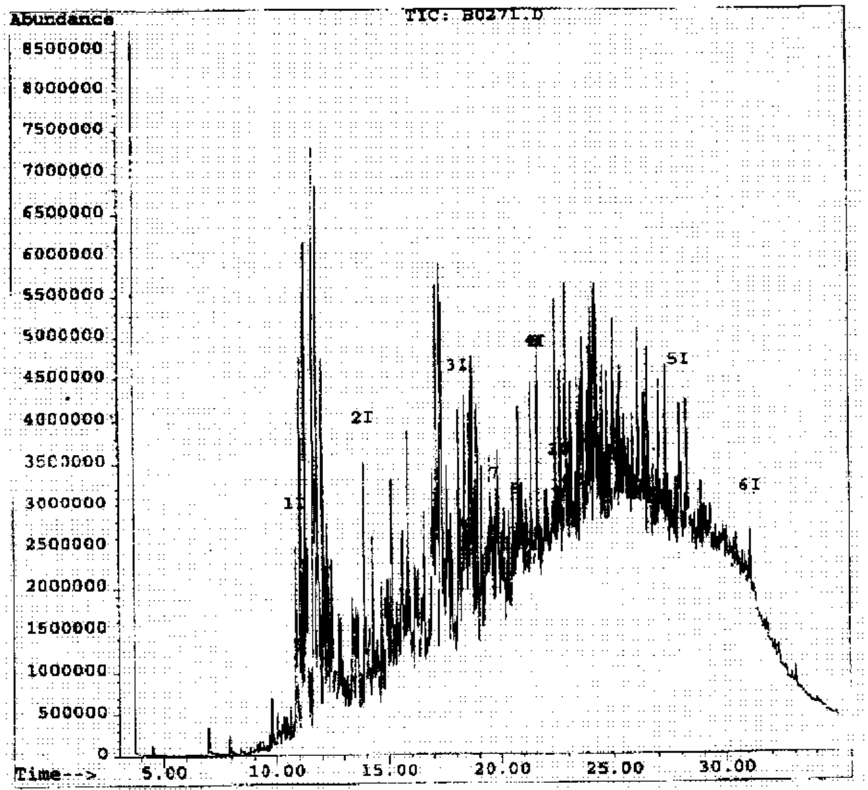
Detailed peak mass matching and relative abundance comparisons of select peaks reveal definitive mass spectral variances between the compounds that allows conclusive identification of either analyte. First off, both compounds have a M + I isotopic peak, however only dibenzothiophene has a very prominent M + 2 signal due to the sulfur. The fragmentation patterns of the molecular ions of the two compounds are nowhere near alike. Both compounds can loose a hydrogen to give M-1 signals, however only benzidine will continue to lose hydrogens giving the M-2 and M-3 peaks. Benzidine can also lose a $-NH_2$ group to generate the M-16 peak at m/z 168 or a NH_3 group, forming a benzyne at m/z 167 (M-17). Dibenzothiophene has no fragmentation pathway to generate either m/z 167 or 168. Extrusion of sulfur from dibenzothiophene gives rise to a prominent peak at m/z 152 (M-32).

The stability of the molecular ion of benzidine is probably enhanced through ring-expansion of one of the aromatic rings to include a nitrogen in a seven-membered aromatic ring (aza-tropyllium ion). Concerted ejection of a CNH_4 unit (M-30) from this ring generates m/z 154. A similar ring expansion, followed by concerted ejection of SCH from dibenzothiophene forms m/z 139 (M-45) as a significant signal that is quite undistinguished in the benzidine spectrum. Other important differences are indicated in Figures 2 and 3, and include m/z 65 and 77 in the benzidine spectrum, while Dibenzothiophene exhibits 69 and 79.

Although the distinguishing features of the two spectra are easy to overlook by eye, it was obvious that the computer spectral matching algorithm was having no such problem, and further investigation focused upon the user generated spectra. This is displayed in Figure 4, along with the spectra from one of the challenged identifications. What was in the sample matched up almost perfectly with what was stored as a spectrum of benzidine from the standard. Using the identification criteria listed above to examine the library spectra led to the inescapable conclusion that the standard used for initial and continuing calibration was dibenzothiophene rather than benzidine.

The retention time of dibenzothiophene is slightly less than that of benzidine, however not so much as to be really startling. Benzidine itself exhibits shifts in absolute and relative retention times as columns are changed in the GC-MS. As it is our habit to replace columns with recalibration, the slight shift in retention time from one initial calibration to the next was unexceptional. The quick visual examination of the mass spectra that accompanied the recalibration failed to detect any differences.

Dibenzothiophene is a naturally occurring substance commonly found in high sulfur crude oils. Discussions with the client revealed that the samples with "benzidine" all came from the soil underneath a storage area where several barrels of high sulfur Venezuelan fuel oil #6 had been placed. The high sulfur levels had made the oil



unacceptable for use in the boilers at the facility. The GC-MS chromatograms contained hydrocarbon hump-o-grams along with the "benzidine" and other sulfur-containing aromatics. As all the evidence was now consistent, the reports were re-issued deleting the benzidine hit.

The investigation was expanded to include examination of the calibration spectra both prior to and after these particular samples were analyzed. It was found that the problem began several months prior to October, 1995 surprisingly in the middle of a supplier's lot number. The problem continued after October, 1995, through the next lot number of benzidine standard purchased from the supplier. It was not until Summer, 1996 and a further lot number change that the spectra reverted back to the correct benzidine mass spectrum.

Figure 1. Chromatogram of sample

ASI contacted the supplier of the benzidine standard and presented them with the above evidence. The supplier was not making any spectral checks upon purchased stock standards as part of their QA program. Only the technically outdated melting point determination was being verified, and it was not being performed as a mixed melting point. There were no ampules of the particular lot numbers available for examination, however the supplier offered to reimburse the cost of the standards.

We went back through every sample analyzed during the year that the incorrect standard had been used. Fortunately we found that no other samples had been reported with hits for benzidine, thus there were no false positives. We are still in the process of doing a manual search of the tape archives for any false negative benzidine hits in these samples. None have been found to date.

How could we have caught the error and prevent it's happening again in the future? The corrective actions we have instituted are to: 1) inject new GC-MS standards under old calibrations prior to changing out the column and re-calibrating; 2) use second source standards to check each new calibration; and 3) closely examine the mass spectrum of each new benzidine standard that is purchased.

The lesson learned? Don't trust anyone's claims or documentation of purity or authenticity. Their acceptance standards may well be different than your own.

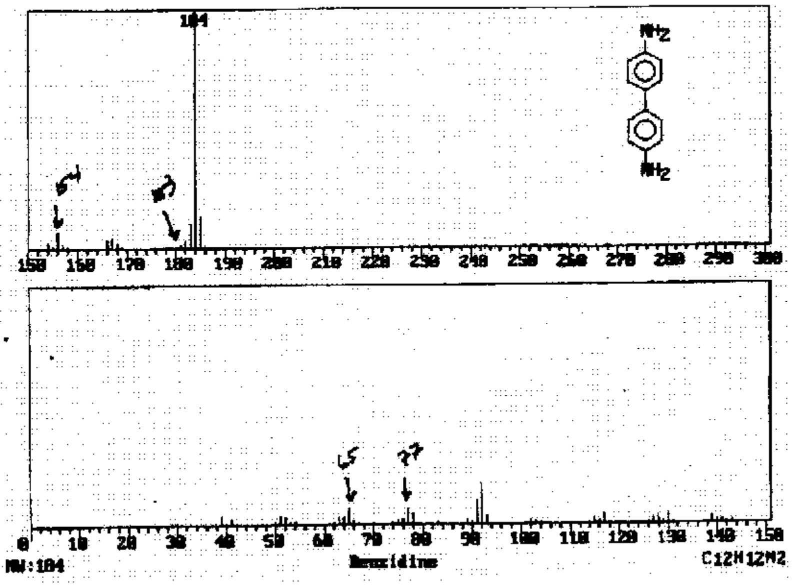


Figure 2. Mass spectrum of benzidine from Wiley-NIST library

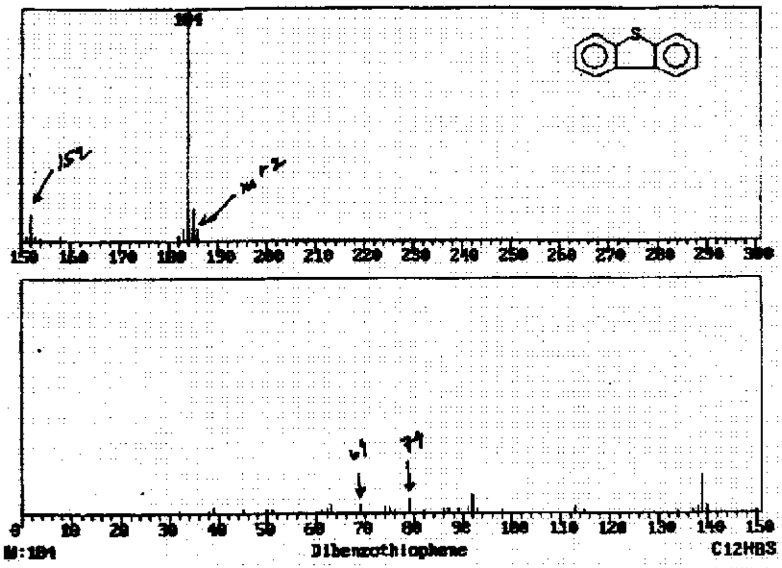


Figure 3. Mass spectrum of dibenzothiophene from Wiley-NIST library

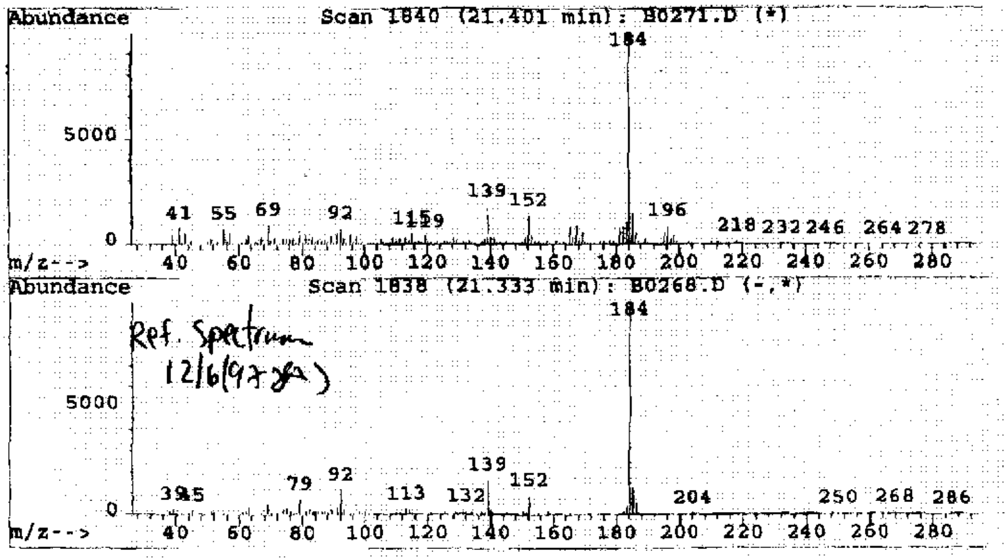


Figure 4. Mass spectra from sample and lab generated library

COMPARISON OF VOLATILE ORGANIC COMPOUND RESULTS BETWEEN METHOD 5030 AND METHOD 5035 ON A LARGE MULTI-STATE HYDROCARBON INVESTIGATION

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ABSTRACT

With the promulgation of SW-846 Update III during June of 1997, elimination of Method 5030 and implementation of Method 5035 have created significant challenges for the regulatory and laboratory communities (US EPA, 1997). Based on historical data, the results for volatile organics in certain sample types using the previously approved direct heated purge technologies were observed to be biased low (Hewitt, 1994). The loss of volatile organics was not observed to be the determinative process of Method 5030 but of the sampling, preservation, and preparatory aspects of the methodology (Hewitt, 1997, Siegrist, 1992). The promulgation of Method 5035 requires training of field samplers and a decision-tree approach to collecting and analyzing samples.