GC-FT/IR and the Analysis of Aromatic Essentials

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Fragrance chemistry requires the separation and identification of many closely related compounds in essential oils, fragrance compositions, and aroma chemicals. Specific identifications may be used by the perfumer to determine the contribution of a component to the final product, to evaluate organoleptic and chemical compatibility within both a formulation and the consumer product, to assure safety requirements, and for quality control.

The infrared spectrum of a sample is a plot of the intensity of light absorbed by that sample vs. the frequency in the mid-infrared range. The spectrum can be considered the fingerprint of the sample, permitting comparison with a known reference spectrum for identification. Failing that (perhaps the reference is not available), infrared can still be useful in elucidating chemical functionality, differentiating isomers, and corroborating structure postulates.

Gas chromatography is the primary analytical separation technique in the perfume industry. An instrument providing the ability to measure the infrared spectra of components of a mixture, on-line, as the components elute from the chromatograph, would certainly be a logical marriage of the two analytical disciplines.

Prior to the advent of Fourier Transform infrared (FT/IR), spectra of GC resolved components were obtained by time-consuming, laborious "trapping" (condensing) of individual GC peaks for subsequent spectroscopic identification.

FT-IR, utilizing an interferometer and computer technology, permitted spectra to be measured more rapidly, precisely, and with greater sensitivity—requisites for use in on-line measurement of GC eluates. Conventional dispersive infrared spectrometers require usually fifteen minutes per scan at 8 cm^{-1} resolution to cover the mid-infrared range. An FT-IR spectrometer, operating at 0.6 seconds/scan can accomplish 1500 scans in fifteen minutes, resulting in an approximate 38-fold increase in signal/noise and a significant decrease in amount of sample needed.

The high precision of FT-IR measurement of spectral frequencies in the absorbance mode makes the final spectrum completely amenable to sophisticated, computerized search of reference spectra libraries.

GC-FT/IR has been used not only to identify the components of complex mixtures, but also to determine organic chemicals in aqueous solution, to identify by-products in aroma chemicals,

REFERENCE
SPECTRUM

1712 0919 0866 LINALYL ACETATE
ENTRY # 47

HQI= 0.17

MEASURED
SPECTRUM

4000.   3500.   3000.   2500.   2000.   1500.   1000.   500.
                        SUB1A PK#10   27.60

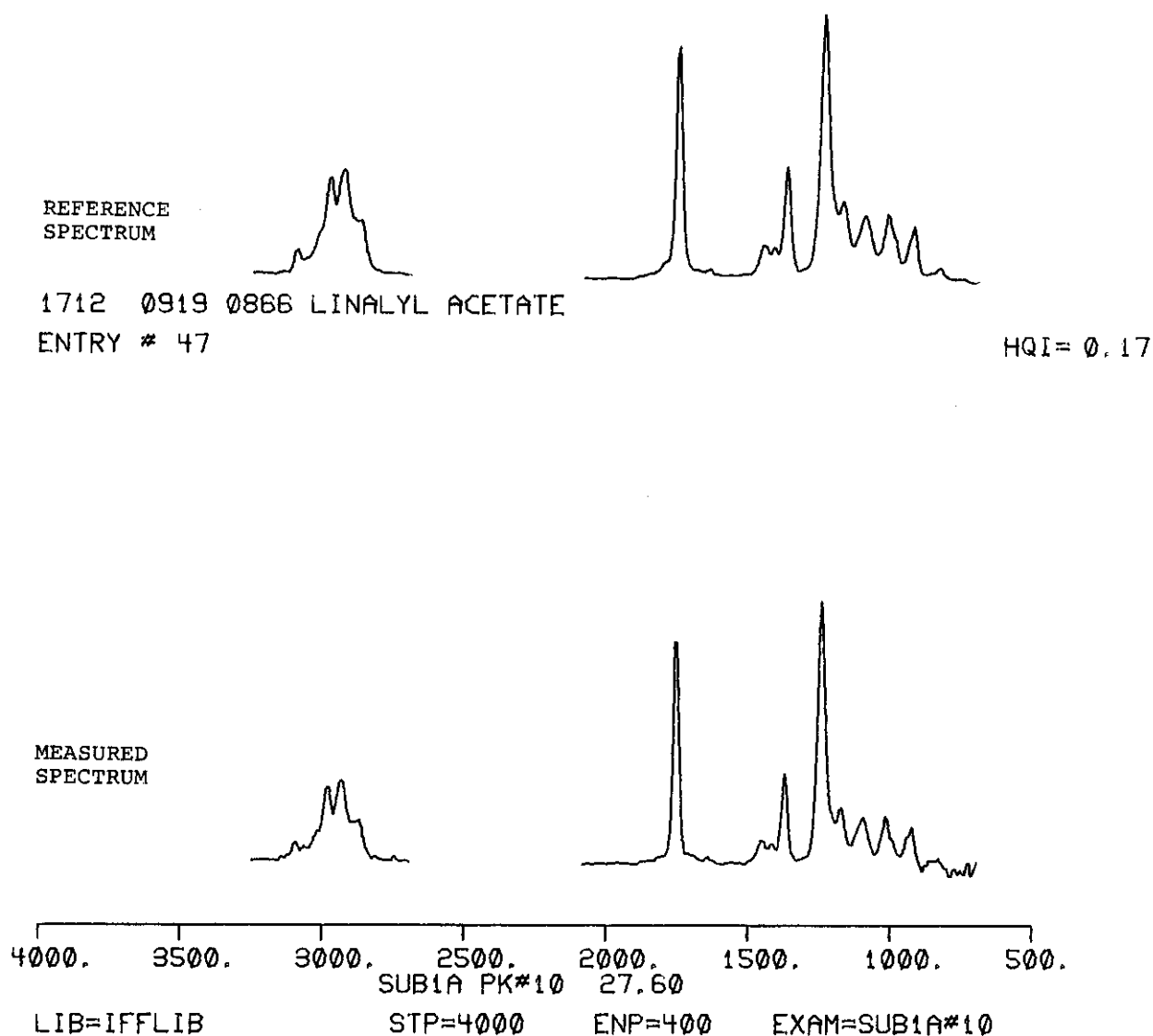LIB=IFFLIB   STP=4000   ENP=400   EXAM=SUB1A#10

Figure 1

and to establish congruency or deviation of similar formulations.

Why GC-IR? The answer lies in its speed of identification, the nondestructive nature of the technique, permitting odor evaluation of the GC peaks concurrent with their identification, computerized data handling, applicability to aqueous solutions, availability of very reliable reference spectra search routines and, in the complementary nature of the technique to GC/MS, particularly for its identification of aromatics and terpenoids.

A GC-FT/IR instrument consists basically of a gas chromatograph, an FT-IR spectrometer, a dedicated computer and ancillary equipment for data storage, display, and print-out. As each GC peak elutes from the chromatograph, it enters the spectrometer where its spectrum is measured as an interferogram, signal intensity detected as a function of time. Computerized Fourier transformation of the interferogram produces the interpretable and familiar absorbance spectrum, signal intensity plotted against frequency.

In our laboratory, the chromatograph is equipped with both a wide bore (60 M x 0.75 mm i.d.) glass column and a fused silica capillary column (50 M x 0.32 mm i.d.). This arrangement gives us the option of using the greater resolving power of the narrow column or the greater sample capacity of the wider column, as dictated by

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 1    2     3        4       5    6      7
UNK#1Ø   SUB1A PK#1Ø  27.6Ø
1    47  Ø.1715  1712   Ø919 Ø866 LINALYL ACETATE
2    89  Ø.3Ø28  9Ø46             5-METHYLENE-4,9-DIME-8-DECEN-2-OL;ACETATE

UNK#11   SUB1A PK#11  3Ø.14
1 31Ø1   Ø.Ø837  87Ø9   1339 Ø9Ø1 DIHYDRO CUMINYL ALCOHOL
2 2752   Ø.3133  87Ø7   12Ø5 Ø843 CARVEOL-T

UNK#12   SUB1A PK#12  35.54
1    45  Ø.Ø553  8755   1127 Ø99Ø GERANYL ACETATE
2    5Ø  Ø.Ø913  8754   1Ø85 Ø967 NERYL ACETATE

UNK#13   SUB1A PK#13  37.41
1 2881   Ø.Ø682  8224   18ØØ 1Ø1Ø COUMARIN
2 2842   Ø.3Ø76  16352            COUMARIN,4-METHYL

UNK#14   SUB1A PK#14  58.Ø9
1   971  Ø.1748  6394   1914 1352 BENZOIC ACID, BENZYL ESTER
2 3Ø88   Ø.278Ø  9997   146Ø 1169 HEXENYL-CIS-3, BENZOATE
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Figure 2. Column 1 = "Hit" Number; 2 = Reference Spectrum Number; 3 = "Hit" Quality Index; 4 = Identification Number; 5 = Carbowax Retention Index; 6 = Methyl Silicone Retention Index; and 7 = Compound Name.

the experiment. The spectrometer has a liquid nitrogen cooled mercury-cadmium-telluride detector, providing an order of magnitude greater sensitivity than room temperature detectors. Spectra are measured between 3800 cm^{-1} and 650 cm^{-1}, at 8 cm^{-1} resolution, Although tens of nanograms of sample per GC peak can provide useful spectra, 100 ng are preferable. Software has been modified to allow the instrument to run unattended, under computer control, for sixteen hours per day (the duration of the liquid nitrogen reservoir). Samples are injected by the auto-sampler, and data is collected and processed by the computer automatically.

Final spectra and search results can be examined either on a terminal screen or in hard copy format, or both. Spectra are usually compared in truncated format, eliminating spectral areas of little or no meaningful content. The "unknown" spectrum and the reference spectrum can be simultaneously displayed (figure 1). A routine has been added to measure the retention index of each component for comparison with reference retention indices listed in the final search report (figure 2).

The GC-FT/IR procedure may be represented as consisting of:

1. Auto Inject—start GC and IR
2. Collect—collect interferograms, co-add scans to give one spectrum per GC peak
3. Fourier Transform—produce an absorbance spectrum

4. Search—best reference spectrum matches per GC peak
5. Print Report—compound names of best matches and their I_Es
6. Plot—reconstructed chromatogram (chromatogram as detected by infrared)
   —functional group chromatogram
   —absorbance spectra
   —reference spectrum vs. unknown spectrum
7. Repeat entire procedure for another sample

Where to now, or what lies ahead? Utilizing current equipment, we can look for an algorithm that includes GC retention indices in the search system. This would allow us to search by IR spectrum, retention index, or both. Coordination of GC-IR and GC-MS search systems would be very valuable.

In the area of instrumentation one can hope for the emergence of more intense energy sources, a higher transmitting light pipe, and improved electronics; all resulting in significant reduction of sample size requirements. We would hope that current research efforts in GC-FT/IR-MS continue and that that type of dedicated instrument appears in the commercial sector.