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NEW TECHNIQUES FOR PYROLYSIS GAS CHROMATOGRAPHY AND POSSIBLE OTHER FORENSIC APPLICATIONS

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General application of Pyrolysis Gas Chroma-
tography (PGC) in criminalistics is related to the
universally recognized need for standardization of
the technique. Utilization of a laser beam for frag-
mentation and Infrared Fourier Transform Spec-
troscopy (IRFTS) for GC peak identification hold
promise for revitalization of PGC. The several
orders of magnitude higher sensitivity of IRFTS
as compared to conventional IR offers potential
applications in criminalistics. Progress in analytical
instrumentation is accompanied by enhanced com-
plexity of the operations which in turn necessitates
increased reliance on computers for data acquisi-
tion and evaluation. The criminalist should be
aware of the consequences and challenges of the
trend.

The popularity and versatility of Pyrolysis Gas
Chromatography (PGC) is attested to by volumi-
nous reference in recent review articles.[1] On the
other hand a profusion of pyrolysers, column de-
signs, and packings makes inter-laboratory correla-
tions and consequently standardization of the
technique difficult. The number of variables is so
great that many publications on PGC have only
limited general value.[2] In fact, a recent report on a
symposium[3] begins with a subtitle "What Is Wrong
with PGC?" The potential of PGC in criminalistics
was recognized some time ago[4] and various appli-
cations have been suggested.[5]

It has, however, been pointed out that the lack
of widespread use of PGC in crime investigations
is related to the absence of standardized experi-
mental procedures and reference PGC "spectra".[6]
One of the major sources of disagreement is the
difficulty of obtaining reproducible pyrolysis tem-
peratures of the sample and maintaining small
temperature gradients. Another common source of
error is the failure to remove traces of solvent when
coating the sample on the filament. A constant
problem is the formation of tars which tend to con-
taminate the pyrolysis chamber and column. The
introduction of the Curie Point (CP) pyrolyser[7]
represented an improvement over resistance heat-
ing with respect to temperature control and heat-
ing rate.[8] While thinly coated films of soluble
polymers yielded good reproducibilities,[9] some of
the disadvantages remained, especially for non-
soluble polymers.

LASER FRAGMENTATION

Recent developments utilizing a laser as the
fragmentation source[10] appear promising for mini-

[1] Mitchell Jr., J. A. and Chin, J., 41, ANAL. CHEM.,
248R (1969); Juvet Jr., R. S. and Cram, S. P., 42, *ibid*,
1R (1970); and Perry, S. G., 7, ADV. CHROMATOGR., 221
(1968).
[2] Levy, R. L., 5, GAS CHROMATOGR., 107 (1967).
[3] Douglas, A. G., 7, *ibid*, 581 (1969).
[4] Nelson, D. F., Yee, J. L., and Kirk, P. L., 6,
MICROCHEM. J., 225 (1962).
[5] Kirk, P. L. and Kingston, C. P., 56, J. CRIM. LAW,
C. AND P. S., 247 (1965); Kirk, P. L., 5, J. GAS CHRO-
MATOGR., 11 (1967); Kirk, P. L., 5, ADV. CHROMATOGR.,
79 (1968); and Kirk, P. L., PROC. SECOND NATIONAL

SYMPOSIUM ON LAW ENFORCEMENT, S. I. Cohn, Ed.
IITRI, 1969, p. 321.
[6] Levy, R. L. and Barney II, J. S., *ibid*, p. 325.
[7] Simon, A. and Giacobbo, H., 4, ANG. CHEM. INT.
ED., 938 (1965).
[8] The method utilizes ferromagnetic materials in the
form of filaments as sample holders. The composition
of the ferromagnetic alloy determines the Curie Point-
temperature at which ferromagneticism is lost. For
example: 60% Co 40% Ni has a CP of +820C while
55% Fe 45% Ni has its CP at 300C. When a radio fre-
quency field is applied, ferromagneticism opposes field
penetration (analogous to ohmic resistance) and the
surface of the sample holder heats rapidly, in approxi-
mately 20 msec, to CP when the resistance is lost and a
constant Curie Point temperature results.
[9] Willmott, F. W., 7, J. GAS CHROMATOGR. Sc., 101
(1969).
[10] Folmer, O. F. and Azarrage, L. V., 7, *Ibid*, 665
(1969) and Guran, B. T., O'Brien, R. J., and Anderson,
D. H., 42, ANAL. CHEM., 115 (1970).

mizing the shortcomings of PGC. Lasers have advantages of shorter heating time, approximately 0.5 msec. The beam can be focused on a limited area of the sample, and temperature can be controled by regulating the energy of the input-pulse. Contamination of and by the sample holder is practically eliminated. A laser pulse with an output of 0.5 joules at 6943Å typically evaporates from nano- to microgram amounts and forms a crater 10 to 100 μm in diameter.[11]

Such quantities are well suited for high resolution columns such as support coated open tubular (SCOT).[12] The resolution power of columns of this type is illustrated by separation of gasoline into approximately 240 peaks.[13]

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IDENTIFICATION OF PEAKS BY INFRARED
FOURIER TRANSFORM SPECTROSCOPY

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It is generally agreed that the superior separation capability of GC has yet to be matched by adequate method(s) of identification. Rather elaborate attempts in theoretical and empirical aspects of GC[14] are of limited value in practical situations. Internal standards are not very useful to a criminalist who usually has to deal with unknown samples. Attempts to interface IR with GC have not been very successful—a rapid scan has to be traded for an unacceptable loss of resolution. A MS-GC combination, while an important step, is not wholly satisfactory, because the correct combination of the molecular fragments can be uncertain. Recent advances in Infrared Fourier Transform Spectroscopy (IRFTS) may, however, go a long way toward solving the problem of on-line identification of GC peaks. This method can produce spectra with speeds up to 1/300 of conventional IR spectrophotometers. Computer signal averaging to boost signal to noise ratio (S/N) combined with extremely high scale expansion enables IRFTS to analyze at nanogram levels.[15]

The spectrometer is based on interference rather than absorption phenomenon. In the conventional spectrophotometer the polychromatic IR radiation is dispersed by a monochromator (prism, grating). A spectrum is then generated by measuring the absorption by scanning a frequency at a time. This process is basically energy wasting and time consuming. IR spectrophotometers capable of 0.5 cm⁻¹ resolution have a slit width of a few mm²; the output of which is dispersed over some 3700 wave numbers (the normal IR range of 4000 to 250 cm⁻¹). In contrast, an FTS spectrometer shines the total IR range undispersed through an apperture of several thousand mm² and collects spectral information in seconds by the use of interference phenomenon. Briefly, in an interferometer, the beam after passing through the sample, is slit into two perpendicular beams; one is sent to a stationary, the other to a moving mirror, after reflection both beams are recombined and sent to a detector (pyro-electric boulometer). If both mirrors would be equidistant from the beam splitter, the reflected radiation would be in phase and the original beam would be restored. However, since the mirror is moving (approximately 0.5 cm/sec) the detector output (interferogram) will be a display of the distance traversed by the mirror vs intensity (energy). The conversion to the familiar frequency vs energy relationship requires Fourier Transform operations over the whole IR range. The lengthy and involved calculations have become practical only by the availability of digital computers. The large energy throughput is only one of the advantages of IRFTS; another is the so called "Fellgett's Advantage" which refers to signal to noise ratio. S/N increases when "looking" at the entire system simultaneously instead of one resolution element at a time. If T is time of the scan and M the number of resolution elements, then according to statistics $S/N = (T/M)^{\frac{1}{2}}$ for conventional IR, and $S/N = (T)^{\frac{1}{2}}$ for IRFTS. For the normal IR, M = 3700 cm⁻¹ and if band width is 1 cm⁻¹ then $[(S/N)FTS/(S/N)IR] = (M)^{\frac{1}{2}} = (3700)^{\frac{1}{2}} = 61$. The advantage in the S to N ratio can be utilized in two ways. If the scan time is limited, resolution can be traded for rapid response. This becomes important when GC peaks of few second duration have to be identified (fast scan). Practically, one could envision a 10 to 1 sample splitter between a SCOT column and flame ionization detector (FID) supplied with high sensitivity electrometer.[16] The FID would indicate retention time by a "blip" while 9/10 of the sample bypasses through an IRFTS cell where simultaneously the IR spectrum is generated. Repeat scanning which

[11] Adams, M. D. and Tong, S. C., 40, *Ibid*, 172 (1968).

[12] Guichon, G., 8, ADV. CHROMATOGR., 179 (1969). Also see note 6.

[13] Sanders, W. H. and Maynard, J. B., 40, ANAL. CHEM., 527 (1968).

[14] HARRIS, W. E. AND HABGOOD, H. W., PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY, 1966.

[15] S. T. Dunn and M. J. Block, AMERICAN LABORATORY, November (1969).

[16] Gill, J. M. and Hartmann, C. H., 5, J. GAS CHROMATOGR., 605 (1967). Also see note 6.

maximizes S/N has many useful applications when IRFTS is used as "amplified" IR (vide infra).

Excellent review papers are available on principles of IRFTS[17] and on digital automation in general.[18]

POTENTIAL APPLICATION OF IRFTS IN CRIMINALISTICS

Pioneering investigations of IRFTS analysis of GC effluents have been reported by Low and co-workers.[19]

, In spite of the fact that the resolution of the instrument used, 18 cm^{-1}, was far less than that presently available, 0.5 cm,$^{-1}$ [20], the results were promising. The several orders of magnitude higher sensitivity suggest many applications of IRFTS where conventional IR fails. A very intriguing application from a criminalist's point of view is the examination of human skin and biological fluids in vivo by IR emission spectroscopy. A substance emits radiation at the same frequency it absorbs, but at ambient temperatures the radiation is so weak that conventional IR instruments usually do not respond. Acceptable spectra can usually be obtained when the temperature is raised above 100C, at which temperature most biological materials undergo degradation. The IRFTS method has yielded skin emission spectra at room temperature which have shown marked differences in spectra of different persons and also between normal and psoriasis affected skin.[21] IRFTS also obtained reflectance spectra from weak sources.[22] Another interesting application is the remote measurement of IR emission spectra of smoke stack gases as a means for polution control.[23] The optical head of the interferometer was installed on a conventional reflection telescope and directed towards the stack 600 ft. away. On a still further extended distance scale, it is known[24] that IRFTS units have been launched in orbits aboard satellites. One can

surmise that detection of rocket exhausts or nuclear explosions might have been a probable task. Finally, on an even more extended scale, ice was discovered in the rings of Saturn by IRFTS.[25]

CONCLUSIONS

Recent developments which utilize the laser as fragmentation source and IRFTS for identification of GC peaks "on the fly" appear to minimize the various shortcomings of PGC which have prevented a more general acceptance of the technique by the criminalist. Additional uses of IRFTS, which is several orders of magnitude more sensitive than conventional IR, may be numerous. Particularly intriguing for the criminalist is the emission mode of IRFTS, which could be possibly used for "fingerprinting" biological materials such as skin, sweat, blood, etc.

If the possibility of the eventual acquisition of a highly computerized and expensive instrument (including two lasers) for a crime lab seems somewhat unrealistic, it may be worthwhile to consider some present day trends. Specifically, if the initial promises of laser fragmentation GC with IRFTS identification of peaks materialize, there will be a demand for such an instrument. As a consequence, PGC (or probably more fittingly FGC—F for fragmentation) of a polymer to be individualized will be discussed in terms of identifiable components (fragments) which in turn can be logically related to a probable chemical structure rather than in terms of retention times and/or peak patterns. While the latter may be sufficient, the former obviously is much more desirable. More generally, there are techniques, which have gained a foothold as a tool in criminalistics, such as neutron activation analysis, which are tied to computerized data acquisition, reduction, and output. The computer can of course collect many more data points than a human, and if properly programmed, can perform a variety of complex statistical operations which improve data and yield a more meaningful output with tremendous saving of time and elimination of human error. This truism is well recognized by instrument manufacturers. Digitized (geared for computer input) analyzers, spectrometers, gas chromatographs, etc., are being turned out in ever increasing numbers. In fact, one gets the impression that if the current trend continues, a direct analog output instrument without digitizers or integrators will be as scarce as a stick-shift family car. Finally,

[17] Horlick, G., 22, APPL. SPECTROSCOPY, 617 (1968); Low, M. J. D., 41, ANAL. CHEM., 97A (1969); and MERTZ, L., TRANSFORMATION IN OPTICS, 1965.

[18] Frazer, J. L., 40, ANAL. CHEM., 26A (1968); Perone, S. P., 7, J. GAS CHROMATOGR. SC., 714 (1969); and Anderson, R. E., *ibid*, 725 (1969).

[19] Low, M. J. D. and Freeman, S. K., 39, ANAL. CHEM., 194 (1967); Low, M. J. D., 1, ANAL. LETTERS, 819 (1968); and *Ibid*, 22, APPL. SPECTROSCOPY, 463 (1968).

[20] *Op. cit.* at note 15.

[21] Low, M. J. D. 22, EXPERIENTIA, 262 (1966).

[22] Low, M. J. D. and McManus, J. C., CHEM. COMM., 1166 (1967).

[23] Low, M. J. D. and Clancy, F. K., 1, ENVIRON. SCI. TECH., 73 (1967).

[24] MERTZ, L., TRANSFORMATION OF OPTICS (1965).

[25] Pilcher, C. A., et al, 167, SCIENCE, 1372 (1970).

the rearrangement of national priorities is forcing natural sciences from their ivory towers into the service for curing the ills of our society. As a consequence, it is not difficult to foresee that forensic science will become increasingly more sophisticated and complicated. In the meantime, the criminalist is well advised to acquire a nodding acquaintance with the principles and techniques of computer based automation of analytical instruments. Terms such as digital electronics, Boolean algebra, assembly language, etc., will become more and more common. In acquiring new instrumentation in the future, it will be extremely important and difficult to optimize the system in terms of real needs, performance, versatility (adaptability to changes and further additions) and obsolescence (a very critical problem at present) in the face of a bewildering variety of systems and manufacturers' claims. Since the instrument systems will be more involved, the mistakes may be costly in terms of unnecessary redundancy (e.g. several instruments with dedicated memories, for one instrument only, when a central memory could be both larger and less expensive). One final note, while confidently predicting increased digital automatization of analytical instruments, it is not an unqualified endorsement. In fact, during the presently occurring analog to digital transition it may be wise to exert restraint in acquisition of both analog or digital instruments until "the dust settles".