at the same oven temperature, allowing the second column effectively to resolve on the basis of polarity difference between the two columns. If adjusted properly, the full peak capacity on the second dimension should now be available for separation, and the total peak capacity should be the product of the first column capacity and the capacity available on the second column at any chosen operating temperature (the second column operates almost isothermally for each individual analysis).

Having a high peak capacity should not be too critical on the second column, but phase polarity or selectivity difference should be carefully chosen.

Peak compression, followed by fast second dimension analysis, results in improved sensitivity of detection; if a 5 s band of effluent from column 1 is compressed and leads to a detected peak width of 250 ms, a 20-fold sensitivity increase should result.

Technically, $C(GC)^2$ with compression in time requires novel procedures. Two systems have been described for $C(GC)^2$ employing band compression. One is based on a rotating elevated temperature modulator which passes closely over the junction between the two columns, incorporating a thick film accumulator section between the columns at the junction. An alternative device employs a longitudinal oscillating cryogenically cooled trap that can collect and focus solute from the first column, then pulse or remobilize the narrow band into the second column.

Given the need for very rapid analysis, rapidly recording detector systems are required.

Peak position in the two-dimension separation space will now be a complex function of volatility and polarity, determined by the individual mechanisms of the two columns chosen, and a full interpretation of the $C(GC)^2$ method is required in this respect. Possibilities for class separation demonstrate that the method has potential for multiresidue and screening applications, and characterization of petroleum products.

See also: **II/Chromatography: Gas:** Column Technology; Historical Development; Theory of Gas Chromatography. **III/Gas Analysis: Gas Chromatography.**

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Pyrolysis Gas Chromatography

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Introduction

The gas chromatographic process is wholly dependent upon solutes having significant vapour pressures at the upper limiting operating temperature of the chosen solvent so that the partition of those solutes between the mobile and stationary phases affords viable separation.

Such a limitation prohibits the analysis of any intractable samples (i.e. potential solutes) unless the means to modify them are invoked.

In order to attain that goal, thermal fragmentation of such samples was proposed with the object of providing volatile products that would yield to conventional gas chromatographic separation. Having identified the resultant products and made the basic assumption that the fragmentation of the sample was complete, one then had to reassemble the jigsaw in order to elucidate the nature, even the identity, of the original sample. In any event, meaningful deduction must be implicit with the base assumption that one is considering primary degradation products, hence, pre-knowledge of the character and/or chemistry of a particular sample is often needed in order to arrive at a definitive conclusion.

Naturally, thermal degradation is a method that requires educated application in that resultant fragments must be of a molecular size that allows sensible interpretation. Obviously, a large number of small fragments are of little value since ultimately most organics will break down to very light hydrocarbons, both saturated and unsaturated, carbon oxides, water and a variety of inorganics of greater volatility, e.g. ammonia, hydrogen chloride, oxides of nitrogen or sulfur.

Although Davison, Slaney and Wragg are credited with the introduction of pyrolysis gas chromatography (PGC) in 1954, there is ample evidence that several workers were developing the method even earlier. It was immediately recognized that the technique was invaluable for the identification of synthetic polymers whose commercial viability depended on suppression of their chemical identities. Thus there was a good reason to conceal the fact that one could not only access competitors' products but learn as much or even more about a particular product than the manufacturer!

Whatever has been said and written about slow pyrolysis is very much open to question. Certain workers have long advocated the use of slow temperature ramps to reveal progressive transitions in the sample. It does not seem unreasonable to suggest that the approach is untenable as homogeneity of the sample is imperilled. Heat transfer within that sample and variable rates of diffusion of any products through unaffected, untransformed, undegraded, affected, transformed or degraded sample cannot be controlled and therefore leaves the question 'what is one actually looking at?' unanswered.

Terminology

It is now agreed that pyrolysis (alternatively, thermal breakdown, thermal cracking, thermal decomposition, thermal degradation or thermal fragmentation) is the transformation of a compound into another substance or substances through the agency of heat alone. Indeed, most pyrolyses are thermal decompositions or fragmentations. Be warned that the formation of larger rather than smaller molecular weight substances is not only possible but, under certain conditions, highly probable (as the writer learnt to his cost very early in the development of the method).

A pyrogram is a chromatogram of a pyrolysate. It was originally used in the sense of a fingerprint and a tentative identity assigned after comparison with a library of known pyrograms which had been prepared under as near identical conditions as was then possible. With the advent of coupled gas chromatograph/mass spectrometer and discriminative mathematical treatments of vast quantities of data, the technique was promoted to a much higher plane but it should be remembered that statistical methods are, on occasion, far from infallible.

Modes of Pyrolysis

Many practitioners still prefer to fabricate their own pyrolysers without a true appreciation of the many factors that influence the results. Both inter- and intralaboratory reproducibilities are affected by introducing self-inflicted intangibles, inevitably reflected in differences of design and operating conditions.

The scale of these problems was highlighted by the outcome of the European PGC Correlation Trials arranged by the Gas Chromotography Discussion Group (now the Chromatographic Society) as long ago as 1968–1975; this was later duplicated on the same samples by Walker *et al.* in the USA. Gratifyingly, the two sets of results were encouragingly similar but, sadly, not identical.

However, despite serious efforts to introduce effective levels of standardization in both apparatus and practice, the technique fell into disrepute. This was principally due to a plethora of home-made pyrolysers, the conditions of their use and, finally, the total inability of inexperienced would-be practitioners to recognize the many pitfalls. Even worse, the method became stigmatized as 'dirty analysis' because of the damning evidence of tarry and/or carbonaceous residues remaining in the pyrolysis zone. The philosophy was that incomplete analysis has little credibility unless an experiment is focused on the observation of a unique independent event which is an indisputable marker of a specific situation.

The Furnace Pyrolyser

The furnace pyrolyser consists of a relatively small, electrically heated, isothermal chamber, preferably integral with the injection port of the chromatograph. Any connecting line should be similarly heated for as short a time as possible to minimize diffusion and

secondary reactions. The furnace itself must have a large thermal capacity to avoid any significant temperature sag upon introduction of the sample and its carrier. It must be so constructed as to allow the sample, contained in a miniature 'boat' or crucible to be introduced through a purged airlock by means of a suitable mechanism.

The most serious drawback is, of course, the presence of a significantly large dead volume where turbulence could cause the pyrolysis fragments to remain in the pyrolysis zone for a sufficient length of time to produce secondary fragments and thus confuse the picture.

The Filament or Platten Pyrolyser

The filament or platten pyrolyser is an electrically heated conductor having a relatively large usable surface area contained in a minimal volume. **Figure 1** shows a recent example of the device which has been fabricated from a piece of Pyrotenax topped by a suitable finned cooling cap carrying a socket accepting a two-pin plug. The filament itself is initially a 2.5 ohmic length of 22 wire gauge platinum, chromel-alumel, nichrome or other resistance wire tightly machine-coiled to an internal diameter of 1.0 mm, tensioned across the central conductor and an extension of the sheath to a 2 ohmic length and spot-welded in place.

Obviously the length of the Pyrotenax barrel must be tailored for a particular injection port and the port itself reamered out so that the annular space between the inner wall of the injection port and the Pyrotenax outer sheath is no wider than 0.2 mm. This is to combat the probability of a back-pressure pulse, for when the pyrolyser is fired at a temperature of, say, 700°C there is a large local carrier gas expansion. Due to the dynamic resistance of the chromatographic column this must be accommodated in the direction of the gas flow to prevent both diffusion and the risk of reverse flow that passes the pyrolysate through the pyrolysis zone a second time with the risk of further thermal modification. This is absolutely essential to observe the terms of good practice. It must also be taken into account that there is a temperature coefficient of resistance which must be accommodated and suitable measures taken to ensure reproducibility.

Temperature control is best achieved by making the filament or platten one arm of a Wheatstone Bridge circuit and adjusting the balance to control final temperature. The system is calibrated by inserting the pyrolyser in a dummy column maintained under the chosen chromatographic operating conditions and observing the melting points of a series of inorganic salts. It should be noted that the current density applied to the filament must be conducive to rapid heat-up for it is essential to attain the pyrolysis temperature in a few milliseconds (if not microseconds) and ensure a hold for, say, no more than 1–2 s by means of associated timer circuitry. In that time the pyrolysis products are on-column and being separated – ideally the thermal profile should be a square wave.

These instrument combinations and their operations, described above, have been tried and tested by the writer in many laboratories throughout the world over many years and have proved easy to handle by laboratory technicians. Pyrolyses themselves are eminently reproducible provided that the sampling

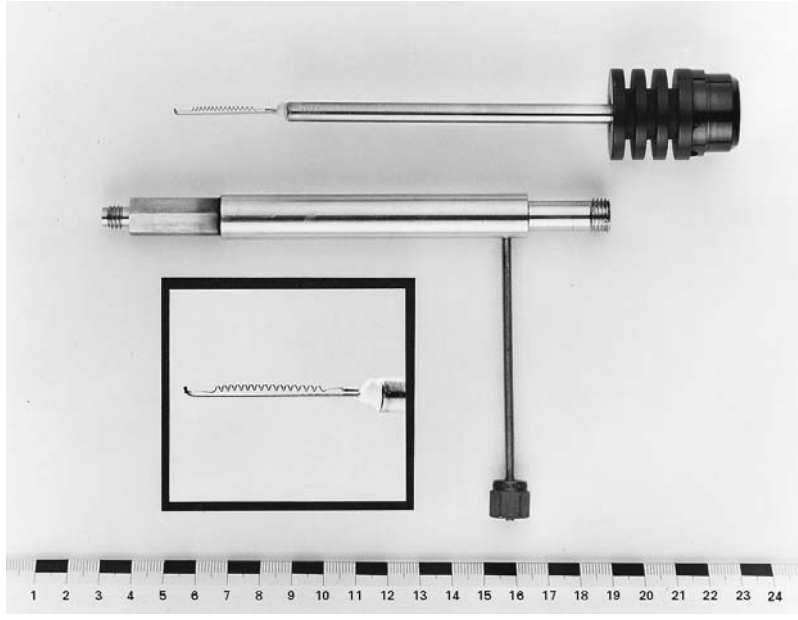

Figure 1 A modern filament pyrolyser together with its modified chromatographic injection port. Inset: detail of mounted filament.

procedure is standardized (see below) and equipment is maintained in as near-sterile conditions as reasonably possible.

At best, the pyrolyser should be cleaned by heating at a higher temperature in an inert atmosphere between every shot. This serves two purposes: first, it removes traces of any residues and second, if cleaned on-column, the completeness of the pyrolysis is verified. In the event that this process is too time-consuming it is better conducted externally or under back-flush conditions.

The possibility of the heating substrate acting as a catalyst has never been completely negated despite a series of standardized experiments conducted by Jones on a variety of metals, both before and after gold-plating. A second hazard is found in the build-up of carbon on the filament itself; this modifies the pyrolysis surface.

The Curie Point Pyrolyser

The adoption of inductive heating by Giacobbo and Simon in 1964 was very quickly recognized to possess many virtues. The most important is found in the fact that final skin temperature (the Curie Point) is a function of the composition of the ferromagnetic conductor when subjected to a given radiofrequency electromagnetic field. Additionally, the skin heating rate is constant for wires of identical cross-section. Moreover, there is no risk of cross-contamination as a 'virgin' wire can be used for each pyrolysis. Sterile storage and handling of new wires is the only precaution necessary.

Table 1 lists the constitutions and Curie Point temperatures of a range of ferromagnetic conductors.

It should be remembered that an energized radiofrequency coil generates an ellipsoid field. In consequence, the Curie wire should be located in such a position that the sample it carries is as near to the centre of the coil as is practically possible. In order to avoid any artefact introduced by an end effect, Jones pointed out that the use of a Helmholtz coil gave a stretched field uniform over a greater length of the coil and hence precise location of the sample became less critical.

A cross-sectional diagram of the built-in injection port receptor designed by Jones is pictured in **Figure 2**.

Figure 3 shows the Curie Point pyrolyser insert in cross-section. Obviously, a simpler, but dimensionally similar insert can be used for conventional liquid sampling so that the integrity of any comparative exercise is preserved.

Figure 4 details the cryogenic focusing unit contained in the oven necessary to counter the inevitable degradation of column performance by the unavoidable presence of an unusually large dead volume which must encourage diffusion as well as other attendant difficulties. A timer/control unit triggers a solenoid valve to close a liquid nitrogen reservoir to build up pressure. A second solenoid valve opens a feed line to allow a jet of liquid nitrogen to play on the front end of the column for 2 s at the moment of pyrolysis. Warm-up of the chilled zone to column temperature to liberate the pyrolysate is near instantaneous by reason of the large thermal capacity of the oven/column assembly. Finally arrangement is made for pressure release in the liquid nitrogen vessel; the cycle is replicated for conventional liquid sampling.

Table 1 Metals and the composition of their alloys which give a usable range of Curie Point temperatures

Metal or alloy (composition %w/w)	*Curie temperature (°C)*
Fe/Ni (78.5% Ni)	200
Fe/Cu/Ni (9.0% Cu/36.0% Ni)	300
Ni	358[a]
Fe/Al (16.0% Al)	400
Fe/Mo/Ni (4.0% Mo/79.0% Ni)	460
Fe/Ni (50.0% Ni)	500[a]
Fe/Ni (68.0% Ni)	600[a]
Fe/Co/Ni (7.0% Co/70.0% Ni)	650
Fe/Si (4.0% Si)	690
Fe/Co/Ni (25.0% Co/45.0% Ni)	715[a]
Fe/Si (3.0% Si)	740
Fe	770[a]
Fe/Co (50.0% Co)	980[a]
Co	1130[a]

[a]The metals or alloys most commonly available drawn as suitable wires. Warning: temperatures quoted are approximate because of impurities and the method of manufacture. Data from Bozorth RA (1951) *Ferromagnetism*. Toronto: Van Nostrand. The help of the British Library, Science, Technology and Business, in this matter is gratefully acknowledged.

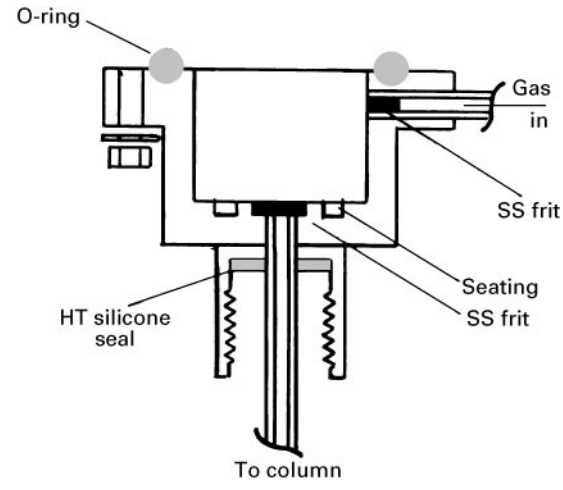

Figure 2 Cross-section of built-in replacement injection port which acts as a receptor for the several inserts (not to scale).

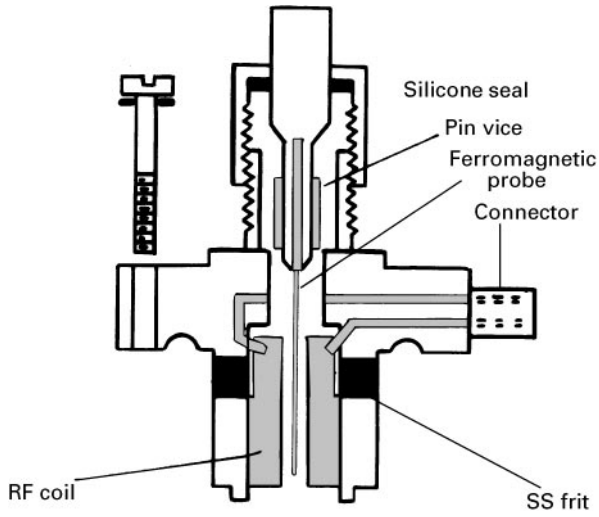

Figure 3 Cross-section of Curie Point pyrolyser insert (not to scale).

Laser Pyrolysis

Both ohmic and inductive pyrolyses are initiated by heating the back of the sample (which can be a serious disadvantage: see Sampling, below). In contrast, laser heating involves surface initiation of the degradation process. **Table 2** compares the pertinent elements of the two processes.

One of the recommended sources of energy is a pulsed neodynium-YAG laser which is mounted in parallel with a neon laser aligned on an identical light path to afford a sight line to aid selection of the required target.

Very rapid heating requires a high thermal flux; perhaps the idea of a pulsed laser is far too simplistic when only the thermal aspects of laser-induced pyrolysis are considered, for the process involves a short, intensive photolysis which radically differs from our present understanding of the pyrolytic process.

A phase-coherent laser beam delivers packets of photons in a nanosecond pulse into the surface of the sample. It should be noted that if the sample is optically transparent, a pigment must be added to provide absorbing centres to promote the ionization of the molecules in the sample surface.

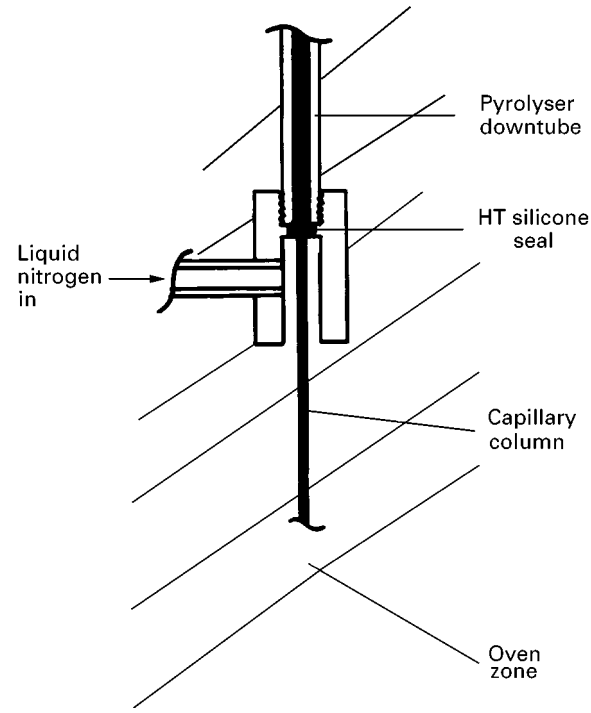

Figure 4 Diagrammatic cross-sectional representation of the pre-column concentration unit (not to scale).

The ionization process can be explained either by electron tunnelling or by multi-photon absorption. After initial ionization, photon energy is selectively absorbed by electrons above the sample surface and the hot electron cloud or laser plume collapses into the sample surface whereupon molecular fragments are pumped into the hot plasma. On termination of the pulse the system rapidly returns to ambient.

The plasma, consisting of unbound electrons, free atoms and those few radicals of unusual stability, is in kinetic equilibrium but when the unbound electrons return to their accustomed atomic states the resultant species quench directly from the plasma and provide an informative series of products. However, other species can arise from thermal scissoring within the solid sample and a further series of products can then result from interaction of those species with certain plasma components.

Table 2 Comparison of two heating processes

	Ohmic inductive heating	*Pulsed laser heating*
Substrate	Metal platten or coil, or ferromagnetic probe	Sample continuum (pigmented if necessary)
Sample	Solution or sonic dispersion	Solid chip or compacted powder
Heating geometry	Sample back	Sample front
Heating rate	10^3 K s^{-1}	10^7 K s^{-1}
Cooling rate	-10^3 K s^{-1}	-10^6 K s^{-1}
Pyrolysis condition	Both in an inert atmosphere	
Time	100–2000 ms	4–800 μs
Limitations	Possible catalytic effect(s). 'Blow-off' due to gaseous products at substrate causing molten undegraded sample to balloon and burst	Heat input/take-up indeterminant. Possibility of plasma reactions and photolysis. Transparent samples need pigmenting

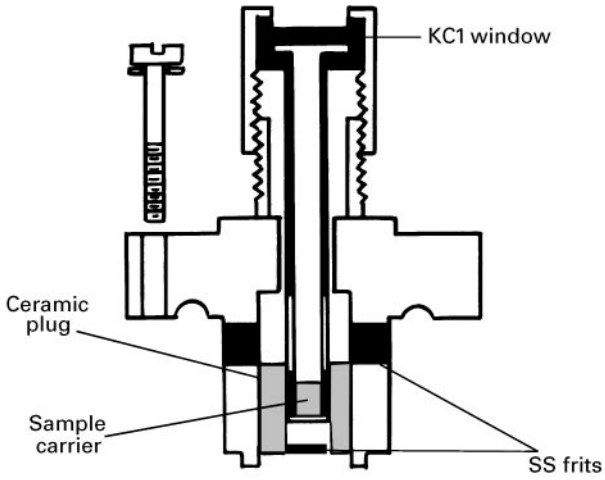

Figure 5 Cross-section of laser pyrolysis cell insert (not to scale).

A laser pyrolysis cell insert for the chromatographic injection port receptor (Figure 2) is shown in Figure 5.

UV Degradation

The only other energy source that has been used in the context of pyrolysis is the UV generator introduced by Juvet, who promulgated its use for stability studies.

The very slow reaction rates associated with time-dependent processes such as the weathering of synthetic coatings, adhesives, rubbers and textiles are in no way compatible with the fundamental concepts of pyrolysis as heretofore enunciated. Therefore the use of UV excitation has shown no advantage over traditional techniques and, in consequence, was abandoned.

Sampling

One of the foremost and, perhaps least appreciated of the initial problems is that of sampling. Sample size and distribution are critical because organics, which comprise the vast majority of potential samples, are invariably very poor conductors of heat.

Jones and Moyles enunciated the thin film concept in 1958. This is based on comparisons of strictly controlled pyrolytic events on the milligram, microgram and sub-microgram scales. Pyrograms of simple substances were demonstrated to be of ever-increasing complexity as sample size increased. The phenomenon was eventually shown to be due to diffusion of degradation products through partially degraded sample and longer residence times in the vicinity of the pyrolysis zone, which led to unwanted secondary reactions. For these reasons it is advisable to work on the nano- or even picogram scale whenever possible.

It should be realized that the most informative evidence leading to an unambiguous conclusion lies in the certainty that all the scissive events viewed are primary reactions (notwithstanding the fact that most primary reactions must be the formation of free radicals which are themselves stabilized by recombination). Therefore it is imperative to regularize the situation as best as possible. That is, the fastest thermal gradient with respect to time within the body of the sample, a condition that is only satisfied by presenting the sample as a very thin film, ultimately as a uni-molecular layer. Unfortunately, the very nature of most samples submitted for pyrolysis prior to gas chromatography is that they are reluctant to form the uni-molecular layers that are theoretically essential. So a compromise has to be made and as thin a layer is distributed on the effective surface of the chosen pyrolyser as is practically possible.

When a sample is soluble in a volatile solvent the deposition problem is ameliorated but immediately poses further problems. What if the solvent lacks wetting power for metallic surfaces? Addition of an amount (e.g. up to 5% v/v) of tetrahydrofuran or dioxan as a wetting agent rarely affects solubilization and overcomes the beading that characterizes a non-wetting system.

After deposition of the sample, residual solvent is best removed in a vacuum oven at a temperature little above ambient. However should the sample be insoluble it is reduced to fine powder by slow freeze-grinding in order to minimize the risk of thermal degradation arising from localized heating due to mechanical friction. It is sonically mixed with a blend of a polar solvent and water containing 1% w/w of a refined natural gum or a purified poly(vinyl alcohol), and then stuck on the probe and dried in the manner already suggested. Conflicting pyrolytic fragments arising from breakdown of the adhesive used can be subtracted from the total pyrogram if deemed necessary; experience, however, has shown that there is little significance in any contribution from the presence of a relatively small amount of an alien material provided that the same routine is used in comparative exercises.

It cannot be emphasized enough that much depends on maintenance of strictly sterile conditions as always.

Applications

The universality of the application of PGC methods has long been a matter of dispute. Without doubt, most disagreement has come from those who have failed both to appreciate and then to observe the basic precepts outlined in this article.

Historically, the method found the greatest initial value in the identification of synthetic macromolecules, while subsequent work by Shin Tsuge in Nagoya led to the elucidation of polymeric microstructures.

There followed studies explaining mechanical strength, cold-drawing properties, film-forming capabilities, cohesion within films and their adhesion to a wide variety of substrates, pigment binding, and the mechanisms of cross-linking processes.

Reiner was the first to appreciate that the difference between a synthetic macromolecule and a biopolymer was merely that of environment. In consequence his work on microbacter and cellular transformations must now be considered to be the foundation for much of today's clinical and pathological practice.

The FOM Foundation group in Amsterdam, under the stewardship of Meuzelaar, expanded the field of application of PGC in parallel with their pioneering work in pyrolysis/mass spectrometry. There, their initial focus was on a broad spectrum of natural polymers.

Wheals, of the British Metropolitan Police Forensic Laboratory, introduced PGC in criminology and developed techniques that formed a basis for standard practice in forensic laboratories. Results are now generally accepted as evidence in many criminal jurisdictions.

The virtue of the very small samples needed for the vast majority of diagnoses has seen adoption of PGC, conducted under very carefully controlled conditions, for the preservation of many art gallery and museum exhibits. For example, deteriorating ancient varnishes and pigments have yielded their secrets and pictures may be cleaned and/or restored without further damage, which will benefit the generations still to come.

Environmental and ecological applications are now coming to the fore. The analysis of occlusions of harmful volatile organics on air-borne particulates has contributed much to our understanding of their significance in the context of respiratory problems.

Bracewell was among the first to develop PGC for the assessment of soil fertility. More recently, De Leeuw graphically demonstrated that reasonably volatile organics such as polycyclic and halogenated hydrocarbons could be excised from very complex matrices (e.g. soils or sediments) by flash evaporation by imposing a millisecond thermal ramp on the sample.

Jones and Vanderborgh employed PGC in conjunction with other pyrolytic studies in their elucidation of coals. They demonstrated that their apparent heterogeneities were due to guest markers of the environments of both the initial debris and the maturation cycle then occluded in a formal cross-linked, spiral double-ladder polymer. An outcome of their work was a proposal for a 'down-hole' mole chromatograph containing a miniature laser pyrolysis cell designed to be lowered into a petroleum exploration, pilot drill hole for real-time *in situ* stratigraphic monitoring of hydrocarbons. Such an approach must certainly be quicker and cheaper than core extraction and subsequent off-site analysis.

In the light of the diversity of applications given here, it is more than apparent that PGC's potential is only limited by the wit and imagination of the educated user.

Conclusions

Despite the early stigma of unreliable and dirty analysis, PGC survived because of the dedication of a small handful of workers who were convinced that most practitioners were to blame for their failures rather than the tool they purported to use.

The method has re-emerged as an active member of the analytical chemist's armoury. This is handsomely substantiated by each successive issue of the *Journal of Analytical and Applied Pyrolysis*.

Material gain has resulted from the adoption of hyphenated instrumentation (e.g. coupling with high speed quadrupole mass spectrometry or Fourier transform infrared spectrophotometry) and has most certainly elevated the status of the technique.

See also: **II/Chromatography: Gas:** Detectors: Mass Spectrometry; Detectors: Selective. **III/Archaeology: Uses of Chromatography in. Art Conservation: Use of Chromatography in. Humic Substances:** Gas Chromatography. **Space Exploration: Gas Chromatography.**

Further Reading

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Sampling Systems

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Introduction

The term 'injection' encompasses techniques used to transfer samples of gases, liquids and solids on to the column for the process of separation to take place. Sample components must be vaporized without decomposition and both major and trace components transferred quantitatively to the column, irrespective of volatility, polarity, etc. During this process, column efficiency must be preserved and band broadening arising from injection (dead space, adsorptive