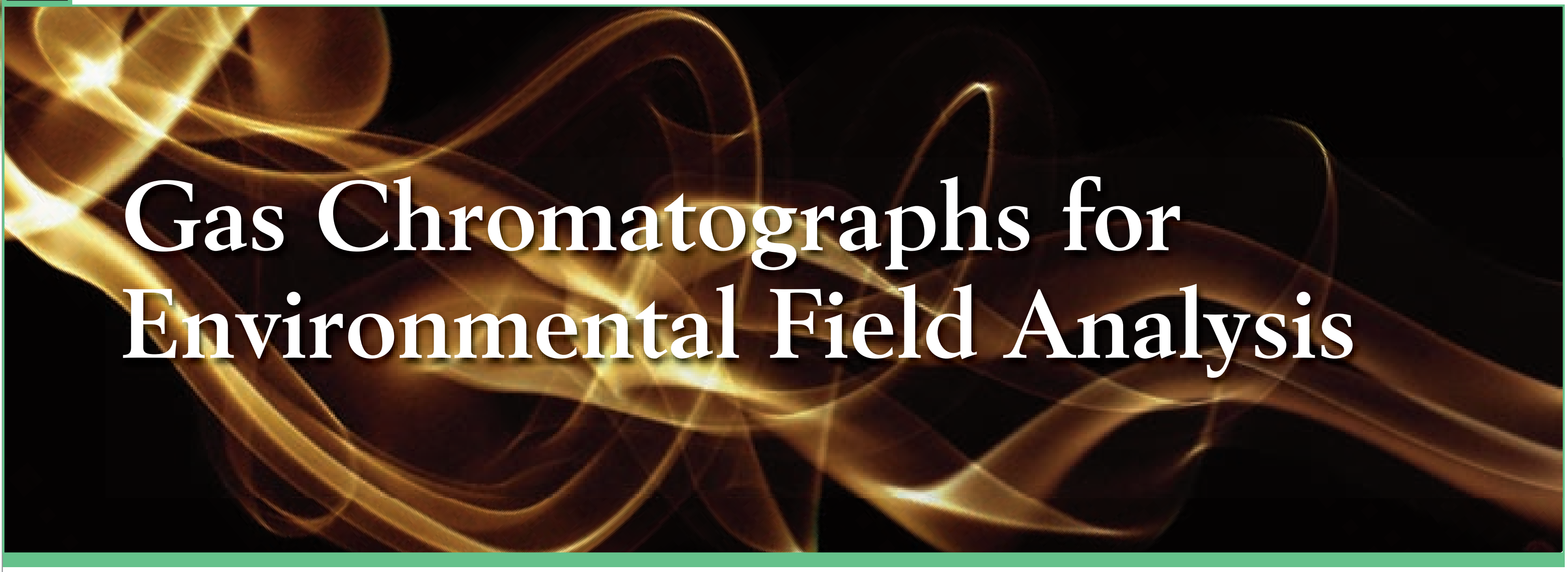

Gas Chromatographs for Environmental Field Analysis

Industrialisation and neglect of clean-up and waste disposal have led to world-wide environmental pollution. Many nations have realised the situation and taken up activities for damage reduction and protection. Concerned laws have been passed and rules stipulated by regulatory bodies. In order to meet the legal requirements, suitable analytical protocols have to be established. Much advancement in analytical sciences has come about as a result of such stringent requirements. Trace analysis of specific molecules in complex matrix is an area that needed to be developed to meet this target. Gas chromatography is the technique that is specially required for organic trace analysis. In this case, sampling holds as much importance as detection. Mobile detectors were developed in order to save time from transportation of samples to distant laboratories. Preservation of analyte sample integrity, prevention of sample degradation and qualitative screening of samples before their selection for elaborate analysis-all could be achieved if the analytical tool is taken to the sample point. This gave a boost to the development of mobile gas chromatographs, portable as well as transportable. Some of them are simple hand-held machines whereas others are sophisticated enough to generate results of laboratory quality. This article highlights a few examples currently available in market.

"Advanced instrumentation allows for field sample analysis, which helps in curtailing loss of sample integrity and delay in sample analysis."

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Environmental Industry is a new concept.

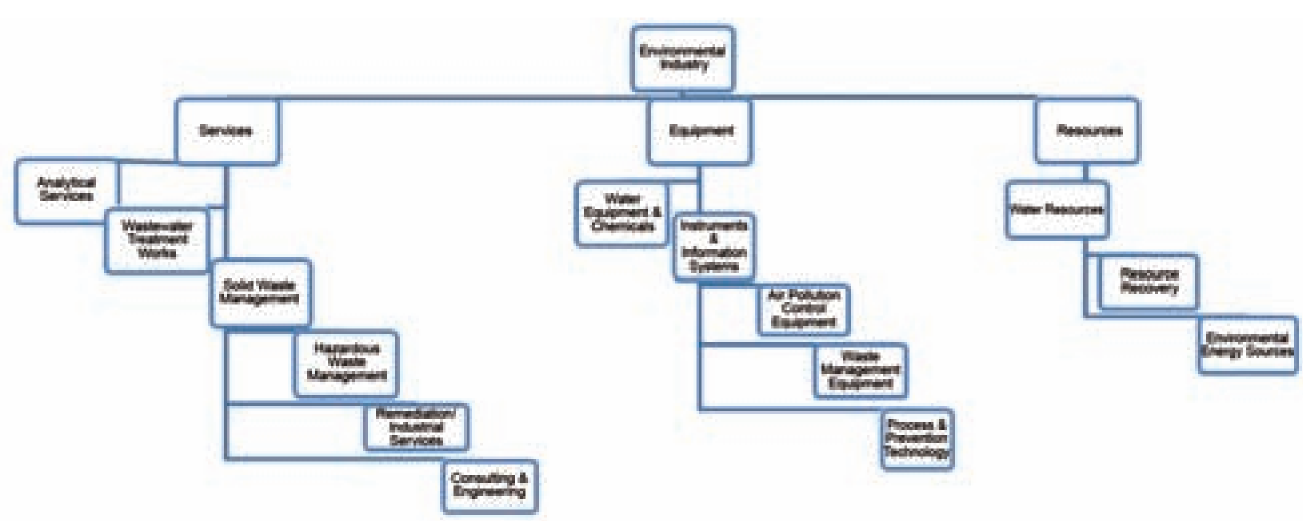
This mainly consists of the industries that affect the environment directly. This industry provides environmental products as well as services. Two distinct phases of the industry can be visualised. The first phase includes public infrastructure services and the second phase includes enforcement of environmental legislation. The environmental industry in the USA is divided into the following segments:

From the classifications given below, it can be seen that chemical analysis of environmental samples is of very high significance for the industry. Choice of the suitable analytical method depends on the nature of the sample as well as the information sought.

Gas chromatography (GC) provides quantitative analysis of volatiles and semivolatiles found in gas, liquid as well as solid matrices. GC finds applications in pharmaceuticals, food, medical materials, pesticides, environmental and petroleum industries, to mention a few.

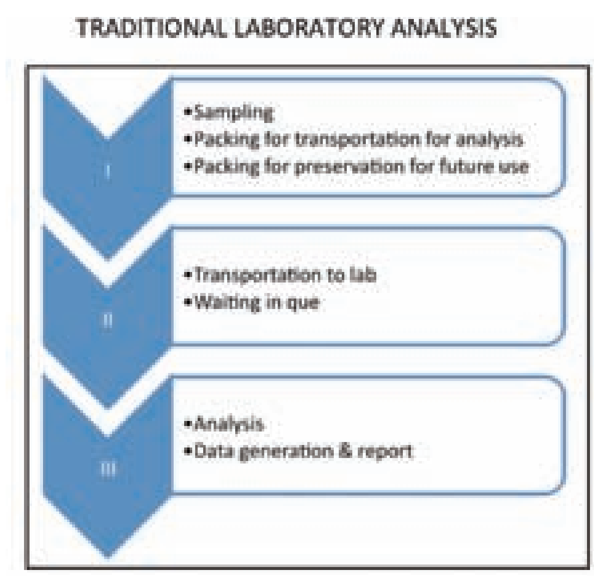
Environmental industries which have the maximum use of gas chromatography for the purpose of bulk composition analysis, carbon monoxide content, sulphurous compounds are landfill operations, biogas, petroleum and fuel, and water treatment plants.

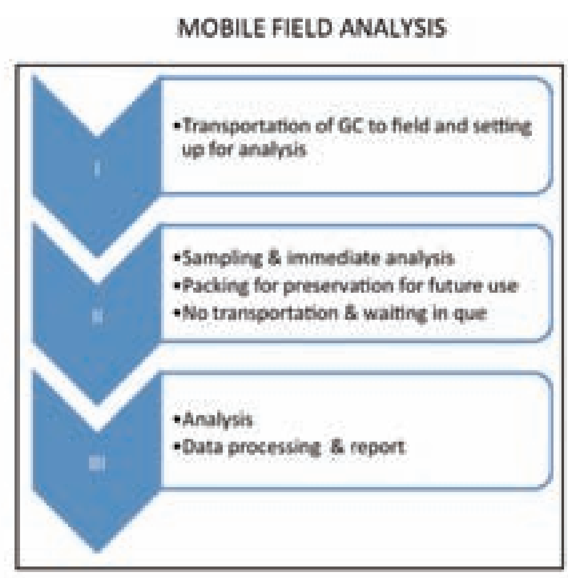
Gas chromatography is the analytical technique of separating and analysing the components of a mixture by volatilising them without decomposition. Gas- solid chromatography developed by Fritz Prior in 1947 and gas-liquid chromatography developed by A.J.P.Martin in 1950, were the predecessors of modern gas chromatography. The key parts of a gas chromatograph (GC) are a sample injector, a separator column, an oven (thermostat) for the separator, a source of inert gas for mobile phase, compatible detector for analytes in the sample and a data system. The past 60 years have seen tremendous developments in this analytical technique. Modifications in injection ports, separation columns, oven design, detector design and optimisation-all have helped gas chromatography in reaching a mature stature. Application



of GC techniques saw tremendous rise in the fields of research, production monitoring, quality check in chemical, petrochemical, pharmaceutical industries, effluent management of industries, forensic science etc. Thus stationary gas chromatographs of different sizes and configurations came about to be developed during the 70's and 80's. Industry requirement demanded the development of **laboratory desk-top and process on-line** as well as at-line GCs. In later years, the requirement of trace analysis and analyte identifications for environmental, legal and security reasons demanded the development of portable instruments. Here also, development was required at two scales- small **portable** handheld instruments for quick, qualitative detection and medium sized **transportable** (taken to location on vehicles) instruments for quantitative on-site analysis.

Advanced instrumentation allows for field sample analysis, which helps in curtailing loss of sample integrity and delay in sample analysis. The steps involved in laboratory analysis and field analysis are as follows:





Volatile Organic Compounds (VOCs)

Naturally occurring methane is mainly produced by methanogenesis which is a form of anaerobic respiration used by organisms that occupy landfill, ruminants and guts of termites. Other than methane, biological sources emit an estimated 1150 teragrams of carbon per year in the form of VOCs. The major constituent of VOCs produced by plants is isoprene which is the building block for terpene. Anthropogenic emission of VOCs is estimated at 142 teragrams of carbon per annum (0.14 million KTPA). The list includes ***solvents*** from paints and coatings, ***chlorofluorocarbons, benzene, methylene chloride, perchloroethylene,*** methyl,tert.butyl ether ***(MTBE),*** octane booster and oxygenated gasoline additive.

Concentration of VOCs in in-door air is found to be several folds higher than outdoor air. Office equipments, wall paints and furnishings, etc are sources of indoor VOCs. VOCs in closed buildings during winter is much higher than during summer months when the building windows and doors are open and indoor air is in contact with outdoor atmosphere. Since exposure to VOCs is harmful for human, animal and plant health, their close monitoring is of utmost importance for remedial and corrective actions. A list of VOCs is given in ref.1

PAHs in environmental samples:

PAHs are polyaromatic hydrocarbons, which are organic compounds with more than one fused benzene ring. They are also called polynuclear aromatic hydrocarbons or polycyclic aromatic hydrocarbons. At least 16 PAH compounds are identified in groundwater[2]. They are known to be toxic and many of them are carcinogenic and cause genetic disorders. OSHA and ASTDR have stipulated exposure limits of these compounds. (e.g.: Air, work place- 0.1mg/m^3 for coal-tar pitch volatile agents, REL♯, water-MCL♯ ~0.0001 to 0.0004 mg/L of PAHs)[3]. Two common approaches exist for the analysis of PAHs in environmental samples. The first one is HPLC method with UV absorbance and fluorescence detection. The method suffers from matrix interferences and the only method of identification is by comparing with retention times of individual standard compounds. The second method is based on GCMS in the full scan mode. Compounds can be confirmed with library stored standard spectra but the sensitivity is at times not sufficient to detect low levels of PAHs. The sensitivity of GCMS measurements can be improved by operating the instrument in the selected ion monitoring (SIM) mode instead of full scan. GCMS of PAHs has a serious limitation. Certain higher molecular weight PAHs show a tendency to get adsorbed on active or cold site of a GC system. This results in lower response and indirectly lower sensitivity of certain PAHs to GCMS analysis.

Portable GC and GCMS hold an important place in chemical and biological warfare detection. Selection of these instruments depends on what is required to be detected. More than the researchers, it is the persons belonging to health and safety departments, hazardous waste management sections and private consultants who are the beneficiaries and potential clients for use of direct on-field GC analysis. There are 'portable', hand-held devices with their own batteries as well as 'transportable' instruments that require more power than what battery can provide. Miniature GCs with field installation capability are also gaining popularity.

The major environmental related areas where portable GC is gaining popularity include:

- **Homeland Security**
  (Chemical Warfare Analysis, Toxic Industrial Chemicals, Explosives)
- **Environmental Monitoring**
  (Volatile Organic Compounds VOCs, in air;
  Semivolatile Organic Compounds SVOCs, in water; accident monitoring; emergency environmental pollution)
- **Forensic Sciences**
  (Drugs, Poisons)
- **Food Safety**
  (pesticide contamination in fruits, grains, flowers;
  food quality testing)

A few examples of mobile gas chromatographs currently available in market and used in environmental industry are presented in the following section.

The model is designed to cater to a selective application area which involves use of GC at worksite or place where the traditional GC cannot be used. The GC works on both AC power line and batteries. The instrument is very compact and fitted in a medium size suitcase. It is equipped with a small cylinder of carrier gas.

Sigma Portable GC

This is the world's smallest gas chromatograph, which is capable of analysing 11 different components of natural gas and digitally publishing the derived parameters such as calorific value, Wobbe-index or density. Model HGC 303 is specifically designed for custody transfer, quality control and other natural gas applications to meet the demands of the expanding natural gas market. This device does not have portability but compact design facilitates field installation. A gas stream containing 11 components can be analysed within 300s using micro TCD and analysis and calculation based on international standards presented (Chromatographic method-ISO 6974, part 4; Heat value calculation method-GPA 2172).

Yamatake HGC 303 Heat Value Gas Chromatograph

Dimensions: 100mm W x 115mm D x 244mm H; Weight: 3.5 kg

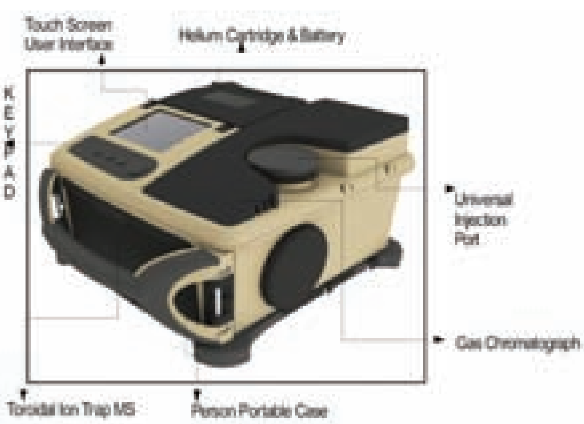
Ultra fast analyser with fully integrated computer. For volatile and semivolatile organics-by choice of capillary columns-capillary columns-DB-5 (semi-VOC) & DB-624 (VOC). Includes rechargeable Li-ion battery power supply and helium carrier gas in a replaceable cylinder. Typical analysis time is 60s and recycle time 30s. Surface acoustics waves (SAW) detector is used. The whole assembly on trolley weighs around 15kg. Detection of analytes at ppb levels is possible.

Working principle:

This is a compact gas chromatograph with in-situ sampling, injection, column separation of analytes. Materials are sequentially eluted from the column and deposited on SAW detector. Deposition results in a change in the oscillating frequency of the resonator, the change being directly proportional to mass. The column temperatre is adjusted on the basis of vapour pressure of the components in the sample.

The SAW/GC was developed by Amerasia Technology Corporation, supported by U.S. Department of Energy (1998). A new company Electronic Sensor Technology (EST) was incorporated to manufacture, distribute and market Model 4100 SAW/GC.[4] This instrument couples a piezoelectric surface acoustic wave (SAW) sensor and a capillary gas chromatograph (GC) with a dynamic particle-vapour sampling interface. The instrument consists of two parts. (a) **Head Assembly** consisting of capillary column, 6-port GC valve, oven trap and SAW detector, (b) **Support Chassis** consisting of helium gas replaceable cylinder, laptop computer and thermoelectric processors. The unit weighed 35 lbs (15.9 kg). Model 4100 is hand-held portable instrument for screening objects, packets, water and air samples. Later versions Model 4300, 4500 & 4600 have (c) **a battery charger** which weighs ~ 3.5kg. Field sampling and analysis of VOCs offers substantial savings above a certain number of samples per year (~100 samples/year in 1992). Using screening method of analysis over commercial laboratory analysis brings down the cost of analysis per sample by a factor of 5. Standard calibration curves are generated and stored in the computer and sample data is compared with the stored data. The laboratory analysis of groundwater pollutants took 50 minutes using GCMS whereas the same sample could be analysed within 2 minutes using Model 4100 SAW/GC in the field.

The TRIDION™-9 GCMS (Torion® Technologies Inc./Irtech) was awarded the most innovative product in 2012 at ExpoLAB 2012, Poland. High speed LTM capillary GC is combined with miniaturised toroidal ion trap mass spectrometer (TMS). It weighs about 14.5 kg, operates on rechargeable battery along with on-board helium carrier gas cartridge. T-9 is portable, fast, and reliable. Analysis time is about 3 minutes. Variety of compounds like chemical warfare agents, environmental pollutants, hazardous materials and food contaminants can be analysed by this instrument. The cost of analysis is low compared to traditional laboratory based GCMS. Sample introduction is by regular syringe injection or CUSTODION® SPME syringes.



Portable-GC-TMS.1260.0.html Dimensions: 38.1cm x 39.4cm x 22.9cm; weight: 14.5 kg including battery

Custodion® Spme Syringe

Solid phase micro extraction (SPME) is a solvent-free technique that combines extraction and concentration of analytes in a simple step. Analytes can be extracted from gases, liquids and dissolved solids.

INFICON HAPSITE Smart Plus Chemical Identification System

This instrument aids in the fast detection, identification and quantification of toxic industrial chemicals (TIC) and chemical warfare agents (CWA) on-site. Hapsite Smart Plus is a person-portable GCMS that gives laboratory-quality results in short time. Use of concentrator for both initial sampling and low-level detection in the ppb/ppt level reduces the time of switch. Special facility of 'Survey Sample Indicator' changes colour to specify when a good sample is achieved by adjusting the probe distance. The analysis results are matched with database of NIOSH & IDLH # and the compounds identified and quantified.

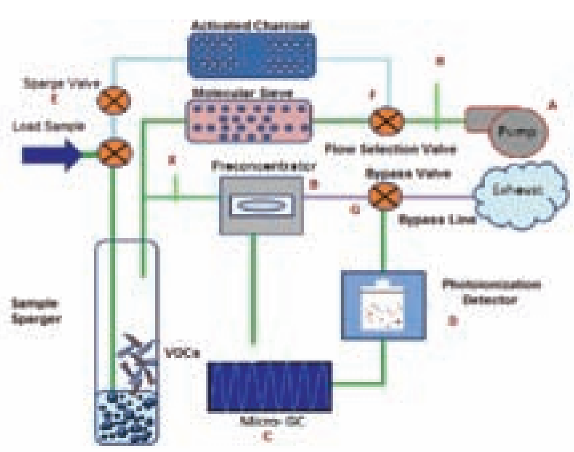
FROG-4000, is a hand-held, portable system from Defiant Technologies.

Defiant Technologies have developed a hand-held portable system, FROG-4000 for the detection of BTEX (benzene, toluene, ethyl benzene & xylenes) and VOCs (volatile organic compounds like TCE, PCE) in water and soil, as well as VOCs in pharmaceuticals. It can be used as a field sample analyser as well as a screening machine in laboratories. The instrument, when set up in the field, gives the appearance of a frog.

FROG-4000 in field analysis

Scrubbed ambient air is used as carrier gas; The instrument weighs just 2.2 kg (5lbs). Dimensions are 10 x 7.5 x 14.5 inches. The microelectromechanical systems (MEMS) fabrication technology has made the miniaturisation of the laboratory instrument gas chromatograph adaptable for field analysis like rechargeable battery operation and no requirement for carrier gases. Performs lab-quality GC analysis of BTEX content in water samples in less than 5 minutes. Method Detection Limits (MDL) for BTEX components are reported as < 0.5 µg/ml with % RSD <20.

The major functional sections are i) the purge and trap (P&T) system and ii) the gas phase analysis system. The P&T system is related to the loading of sample, sparging of liquid samples to release VOCs, and introduction of gas phase analytes to the analyser system. The gas module is the heart of FROG-4000. It consists of miniaturised preconcentrator, microGc and photoionosation detector.



Gas phase analysis system components

A- Diaphragm pump, circulates carrier gas through the system

B- Preconcentrator, collects and injects VOCs into the GC Column

C- Micro gas chromatography column, separates VOCs

D- Photoionisation detector, 10.6 eV Lamp, detects VOCs

E- Sparge Valve, directs pump flow into sparge bottle to purge out VOCs from sample

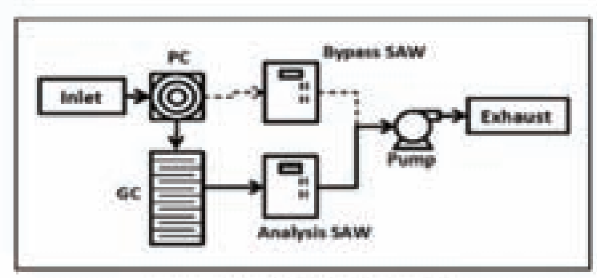
F- Flow Selection Valve, determines flow direction during SPARGE or ANALYSIS mode

G- Bypass valve, allows VOCs to get collected on preconcentrator (B) and bypass micro-GC (C) and PID (D)

H- Pump split, provides a small leak in pump flow for improved flow control

X- Injection split, provides a small leak to prevent rebound injection

Canary-Three is an intelligent handheld GC/SAW system from Defiant Technologies for monitoring liquid and semivolatile organic compounds (SVOCs). The smart sampling system ensures selection of appropriate sample volume depending on the analyte concentration so that the detector is not overloaded. Canary-Three has a detector in one pathway for rapid screening and another detector in the pathway containing a microGC for more detailed analysis. The two-detector system enables quick analysis of samples.



Canary-Three™ System Schematic

Liquid sample injection port, Canary-3

Cycle Time: 2 minutes,

Dimensions & weight: 12 x 6 x 4 inches, 3.7 kgs

Carrier gas: Ambient Air

Can- analyse selected and programmed chemicals in both liquid and air samples

Micromachined (MEMS) column and SAW detector

Choice of 3 thermal desorption preconcentrator inlets for samples of different volatility. For high volatiles, a torturous path preconcentrator having very high surface area to volume, finned structure that supports sorptive coatings is designed. The coatings are sol-gels, which provide high capacity, selective retention, and low mass. Upon heating, the low thermal mass releases the analytes in a plug to the GC. The column is a work of micromachined art. It is a three-layer sandwich called the LIGA-GC. The center is a nickel coupon with an array of holes. The "bread" is a

LIGA machined serpentine that connects the holes in series to give a 1-m column the size of a dime. For 10 m of length, the column is layered to form a cube, smaller than a sugar cube. Detection is with a delay-line surface acoustic wave microbalance resonator, which is about the size of a dime. The resonator is coated with a thin sorptive polymer. The sorption/desorption process produces a signature that is unique to each analyte. Two cells are used: One is for reference, and the other monitors the column effluent. A microprocessor converts the difference to a signal that is proportional to the detected mass. Detection limits are low picogram levels.

Quadrex SRI Model 310C

Quadrex SRI Model 310C is reportedly the smallest custom-configured, transportable, full featured GC available presently. Foot print dimensions are 12.5"W x 14.5"D x 13"H. The instrument can be used for both field and desk-top applications. It provides ambient to 400°C temperature programming capability, multiple ramps, choice of 4 detectors and 2 injectors. The fast cooling system enables high sample throughput. Options of standard detectors like FID, PID, ECD, DELCD, TCD, NPD, FPD & HID. Preconfigured and custom-featured portable GCs are made by Quadrex. As in the case of full-fledged laboratory gas chromatographs, accessories such as gas sampling valves, purge and trap, headspace and methaniser are available for fitting with the bigger models of Quadrex portable GCs. Environmental and BTEX samples can be analysed. For laboratory or mobile field testing of environmental samples, Environmental GC is one of the good configurations. Equipped with purge and trap, PID and FID/DELCD combination detectors, *certification quality data* for EPA methods 8010, 8015, 8021, TO-14 and many others can be generated. DELCD is very similar to ECD in sensitivity but is much more selective to halogens and unresponsive to oxygen. SRI DELCD differs from traditional wet electrolytic conductivity detector in that it neither uses a solvent electrolyte nor a nickel reaction tube and the reaction products are detected in the gas phase. In the high sensitivity mode, DELCD is capable of detecting pictogram levels of halogen containing compounds.

Agilent LTM II 5975T GCMS System

Although GCMS has long been considered as the most important instrument for environmental laboratories, potential of their field application has not been exploited fully. Design modification in terms of ruggedness and miniaturisation are necessary to put the instrument to field use. Low thermal mass fast GC is the most recent technique and field instruments are being designed based on this principle. E.g. LTM series II rapid heating/cooling technique by Agilent. The technology combines a fused silica capillary column with heating and temperature **sensing components wound around it, which gives faster temperature ramp rates. Compared to conventional GCs where the oven is heated** by air bath technology, direct resistive heating of capillary in LTM

technology enables fast heating and cooling, thus reducing the analysis cycle and permitting high sample throughput.

Agilent LTM II 5975T is the first commercial transportable GCMS system that delivers the same quality of results as the high-end 5975 GCMSD instruments. The dimensions of the basic instrument without any accessories is 41 cm H x 60.8 cm W x 65 cm D; 31.8 kg

Agilent LTM II 5975T loaded on a vehicle

1.8 to 1050 µ mass range; rapid heating (1200°C/min) and cooling reduces the cycle time of analysis.

The basic operation software used for GCMS analysis is Agilent MSD ChemStation software.

Applications:

- Rapid field analysis of VOCs with the Capillary Trap Sampler (CTS) and Thermal Separation Probe (TSP)
- Field analysis of VOCs in ambient air by Mini Thermal Desorber (TD)- detect more than 60 VOC compounds including CFCs, hydrocarbons and aromatics in one injection with less than 15 minutes of cycle time.
- VOCs in drinking water by 5975T in conjunction with 7694E headspace sampler. 54 target VOCs in 9 minutes following EPA Method 542.2
- Chemical Warfare agents (CWA) ; fast analysis by enhancing GC column heating and helium flow rate
- Pesticides in vegetables analysed with 5975T using Deconvolution Reporting Software (DRS) to reduce the ChemStation data handling and identify compounds with Retention Time Locking (RTL) Pesticide Database.
- PAHs in soil, when extracted with Agilent Bond Elut QuEChERS kit, reduced preparation time to 20 minutes, and DRS report generation in 30 seconds.

Summary:

Gas chromatography became the work-horse for vapourisable organic compounds analysis by 1980s. Petroleum refining and chemical industries made the maximum use of this technique. Concerns of trace impurities in pharmaceuticals, food and drinking water led to improvement in the sensitivity and detection limit of GC techniques. Last few decades of the twentieth century saw developments in preconcentration techniques, separation techniques, column designs and detector concepts. Environmental concerns & law enforcements increased by the close of the millennium, which led to the development of sensors and detectors that can give indication about hazardous materials at point-of-source. Thus, the turn of the century is seeing a flurry of activities in mobile detector technology. Specific sensors may have better detection capabilities but they are limited in applicability. To detect and analyse specific entities in complex matrices, separation techniques are also important. This has given boost to gas chromatography, which can use selected detectors as per the requirement of analysis. The necessity for analysis of trace organic compounds at point-of-source has led to developments in mobile gas chromatography. The progress in electromechanical miniaturisation, separation techniques, electronics devices and computation, has helped in downsizing gas chromatographs. Portable and transportable gas chromatographs are presently getting wide acceptance in environment monitoring. Examples of a few mobile GCs presently available commercially are discussed in this article.

Annexure

REL ♯ - Recommended exposure limit-recommended air-borne exposure limit for coal-tar pitch volatiles, (cyclohexane extractable fraction), averaged over a 10-hour work shift

MCL ♯ - Minimum Contaminant Level

NIOSH & IDLH # - National institute for Occupational safety and Health & Immediately Dangerous to Life or Health

Detectors for SRI Environmental and BTEX GC

FID-flame ionisation detector, PID- photoinisation detector, ECD-electron capture detector DELCD-Chlorine/Bromine selective Dry Electrolytic Conductivity Detector, TCD-thermal conductivity detector, NPD-Nitrogen-Phosphorus detector, FPD-flame photometric detector, HID-helium ionisation detector.

Analytical Methods

EPA Methods

8010 – Halogenated volatile organics by gas chromatography
8015 - Nonhalogenated volatile organics by gas chromatography ; Total Petroleum Hydrocarbons by GC/FID
8021 - Halogenated volatiles by gas chromatography using photoionisation and electrolytic conductivity detectors in series: Capillary Column Technique
TO-14 – Volatile organic compounds in ambient air using Summa canister sampling and gas chromatography (GC) analysis

ISO Methods

ISO 6974-4:2000 Natural gas -- Determination of composition with defined uncertainty by gas chromatography -- Part 4: Determination of nitrogen, carbon dioxide and C1 to C5 and C6+ hydrocarbons for a laboratory and on-line measuring system using two columns

GPA Methods

GPA 2172-09 Calculation of Gross Heating Value, Relative Density, Compressibilty and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for custody transfer. STANDARD published 01/01/2009 by Gas Processors Association

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