# RAPID ON-LINE CONTROL OF MULTICOMPONENT CHEMICAL STREAMS BY PROCESS MASS SPECTRAL ANALYZERS

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الخلاصة :

إن التقدم السريع الذي شهدته تقنية الكمبيوتر وطريقتا فصل مركبات الغاز بالإمتزاز وقياس الطيف الكتلي المستخدمان معا قد جعلت من الممكن استعمال بعض أجهزة قياس الطيف الكتلي كمحللات لمركبات السوائل الكيميائية متصلة إتصالاً مباشراً بخطوط التشغيل ، وهذا ما يجعل من الممكن تصميم حلقات مراقبة ووضعها مع مركبات السوائل كمتغيرات أثناء التشغيل .

إن المزية الرئيسية لاستعال محلل طيفي كتلي يؤدي مهمته أثناء التشغيل هي السرعة الكبيرة التي يتم بها التحليل (قد يأخذ زمناً لا يتعدى ١٠ ثوان أو أقل) ، وقابليته لمعالجة السوائل الكيميائية التفاعلية ذات العناصر المتعددة في درجات حرارة عالية . ويناقش البحث مزايا أخرى إضافة إلى تصميم المحللات وتطبيقاتها الممكنة وتطوراتها المستقبلية .

### ABSTRACT

Rapid advances in computer technology and in combined gas chromatography/mass spectrometry have made certain mass spectrometers viable choices as on-line analyzers of the compositions of chemical streams. This makes it possible to design and implement control loops with stream compositions as realtime variables.

The main advantages of a process mass spectral analyzer are its speed (in the order of 10s per analysis or better) and its ability to handle reactive multicomponent chemical streams at elevated temperatures. Other benefits are discussed together with analyzer designs, possible applications, and future developments.

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#### **INTRODUCTION**

For chemical processes, the direct use of stream compositions as control loop variables is highly desirable. In addition to the better establishing and implementation of production criteria, compositional measurements in real time are also important in the formulation of strategies for optimizing energy usage. Pollution and occupational safety considerations are additional incentives for incorporating compositional measurements in process control loops. On-line control of process streams by means of inference from physical measurements such as pressure and temperature necessitates prior modeling involving not only delays and additional labor, but also approximation errors that are difficult to avoid.

Mass spectrometers are inherently ideal for on-line monitoring of multicomponent chemical streams. In addition to high sensitivity and specificity, mass spectral data are highly compatible with computers. More importantly, however, the response time of such instruments can be extremely fast, in the order of 10s per analysis or better. This is one to two orders of magnitude faster than a process gas chromatograph. The fast response time makes it possible, for example, to optimize feed streams on a continuous basis. In a typical commercial plant, annual savings from feed control alone can pay for initial investment many times over.

An important advantage of the process mass spectral analyzer is its capability to handle highly streams reactive multicomponent at elevated temperatures. This is the area where the process gas chromatograph often experiences severe limitations. When reactive chemicals are present in the target stream, the accuracy of gas chromatographic measurements deteriorates rapidly because of the relatively long lag time between sampling and detection. In addition, when components in the target stream have diverse chemical properties, multiple process gas chromatographs are necessary either to shorten the analysis time or to measure the entire stream composition. The use of multiple units largely offsets the benefit of using process gas chromatographs as lower cost analyzers.

### PRINCIPLE OF PROCESS MASS SPECTROMETRY

Process mass spectrometry differs from conventional mass spectrometry in that the latter is often used to identify and determine unknown compounds while the former is usually applied to measure known chemicals in a process stream.

To identify an unknown compound, conventional mass spectrometry makes use of the entire mass spectrum of the compound, consisting of 'mass ions' whose mass distribution pattern serves as a fingerprint. These mass ions represent charged molecular 'fragments' formed under electron impact conditions in the ion source of the mass spectrometer. The fragment ions are always reminiscent of the chemical structure of the original molecule.

In a multicomponent chemical stream, the presence or absence of a particular chemical can be determined via the presence or absence of mass ions uniquely characteristic of the target compound. The ion current of these characteristic ions, as measured by mass spectral ion detectors, is directly proportional to the amount of the target component in the stream. The selective measurement of the characteristic ions of interest is the essence of process mass spectrometry.

The concentrations of target components in a stream are determined from the measured ion currents of characteristic ions corrected for overlapping contributions as well as for component sensitivity factors prevalent under the particular instrumental conditions [1]. For an *n*-component stream with concentrations  $c_1, c_2, \ldots, c_n$ , the measured ion currents,  $I_i$ , of *n* characteristic ions are given by:

$$I_{1} = C_{1}F_{11} + C_{2}F_{12} + \dots + C_{n}F_{1n}$$

$$I_{2} = C_{1}F_{21} = C_{2}F_{22} + \dots + C_{n}F_{2n}$$

$$\vdots$$

$$\vdots$$

$$I_{n} = C_{1}F_{n1} + C_{2}F_{n2} + \dots + C_{n}F_{nn}$$
(1)

where  $F_{in}$  represents the contribution from each of the

n components to the characteristic ion i, if any, and

$$C_i = c_i r_i \tag{2}$$

where  $r_i$  is the sensitivity factor of component *i*. In matrix notation, Equations (1) are given by

$$\mathbf{I} = \mathbf{F}\mathbf{C}.\tag{3}$$

#### ANALYZER DESIGN

The primary objective of, and hence requirements for, a process mass spectral analyzer are fundamentally different from those of a laboratory mass spectrometer. A laboratory mass spectrometer is intended for varied applications, and therefore requires versatility. A process mass spectral analyzer, on the other hand, is dedicated to perform specific analytical tasks continuously over an extended period of time. This requires minimum supervision and long-term reliability in the plant environment. These considerations are important in the design of a mass spectral analyzer for process control.

Conventional mass spectrometry usually identifies and measures all mass ions formed in the ion source. These data are stored in a computer data system, and can be regenerated in various formats by data reduction steps for different applications. In process mass spectrometry, however, in order to determine the composition of a well-defined stream for control purposes, only measurements of mass ions that are uniquely characteristic of the stream components of interest are needed. This can be accomplished either through instrument hardware design or by a special algorithm implemented by a microcomputer.

Figure 1 illustrates the hardware design of a mass spectral analyzer that separates and measures a fixed number of preselected characteristic ions [2]. Such a design is reminiscent of a totally automatic mass spectral analyzer deployed during the Viking unmanned spaceflight to Mars. The stream components are leaked into the ion source where mass ions  $(A^+, B^+, \ldots, \text{ etc.})$  characteristic of these components are first formed. These mass ions enter into the ion analyzer as a focused ion beam, and are subsequently deflected in the magnetic field and collected by Faraday collectors. In a fixed magnetic field, the deflected path of an ion with specific mass-tocharge ratio is known. A series of ion collectors can therefore be prepositioned to collect target ions. The design is simple, requires little instrumental adjustment during operation, and is ideal for a real-time control loop in a plant environment. The major disadvantage



Note. Mass ions of interest are deflected in the analyzer magnetic field and reach prepositioned ion collectors for detection. Figure 1. Process Mass Spectral Analyzer of Fixed-Field Design

is that it lacks versatility and cannot be readily used to measure ions other than those preselected. Another disadvantage is that the number of components that can be monitored is usually limited to eight or less.

The fixed-field mass spectral analyzer is more useful for simple petrochemical streams. For example, critical streams in an ammonia plant can easily be monitored by a single mass spectral analyzer. Exit streams from the secondary reformer and methanator, feed streamto-ammonia converter, and ammonia converter effluent can be analyzed at 10 s/stream or 40 s/cycle or better [2]. This not only maximizes ammonia production by constantly adjusting the hydrogen-tonitrogen ratio, but also increases operation efficiency--leading to a significant saving in energy. Other chemical streams, such as effluents from ethylene oxide production and vinvl chloride from chlorination or oxychlorination of ethylene, have also been monitored similarly [3]. In one case, a single mass spectral analyzer was able to monitor and control a tworeactor system originally monitored by a combination of an oxygen analyzer, two on-line gas chromatographs, and three on-line infrared analyzers [2]. The analysis time was reduced from 20 min to 9 s.

The fixed-field mass spectral analyzer, however, is limited when the target stream is chemically more complex and the number of stream components of interest exceeds the number of ion collectors available. When the number of target ions exceeds 10, it is usually no longer convenient to use an array of collectors to detect ions deflected from a fixed field. Instead, alternative means are necessary to detect mass ions selectively.

Figure 2 illustrates a quadrupole mass filter commonly used for selective ion monitoring. The quadrupole mass filter consists of four parallel rods with RF and DC voltages applied to opposite rods, one pair of rods being  $180^{\circ}$  out of phase with the other. For given RF and DC voltages, only ions of one particular mass-to-charge ratio, m/e, can pass through the center of the assembly and reach the ion detector. A full mass spectrum can be obtained by sweeping a voltage ramp at a fixed RF/DC ratio. Alternatively, any number of mass ions can be monitored selectively simply by stepping up the voltage through preset levels so that only ions with values of m/e of interest are detected.

A quadrupole mass spectral analyzer is well-suited to a process control environment. It is of lower cost than a scanning magnetic sector type mass spectrometer. In addition to its ease and rapidity in monitoring selected ions, a quadrupole mass filter has a linear mass scale which is easy to calibrate. It does not require the use of high voltages to accelerate ions,



Note. At given DC and RF voltages, only mass ions of a specific mass-to-charge ratio can pass through the quadrupole filter in the resonant state.

Figure 2. Quadrupole Mass Spectral Analyzer

as does a scanning magnetic sector type instrument, and hence it is much easier to control electronically. More importantly, it is better able to control multicomponent streams than a fixed-field instrument since it is not limited in the number of ions that can be monitored.

Quadrupole mass spectrometers have long been used as residual gas analyzers for light gases [4,5]. Their application in the chemical industry as on-line analyzers has, however, been limited in the past. In recent years, quadrupole process mass spectral analyzers have become a more viable choice [6–11], mainly as a result of rapid advances in computer technology that reduce the level of technical support required in an operational environment. In addition, technological improvements in combined gas chromatography/mass spectrometry have also had an impact on the progress of process mass spectrometry.

### REACTIVE MULTICOMPONENT CHEMICAL STREAMS

There have not been many published reports on the application of process mass spectral analyzers to the on-line control of complex streams. The use of quadrupole mass spectral analyzers in the pharmaceutical industry for the on-line control of continuous fermentation processes has been reported recently [7,8]. Efforts to develop process mass spectral analyzers to control reactive multicomponent chemical streams at elevated temperatures have been reported in the patent literature [9, 10].

The incentives to use on-line analyzers for reactive streams are many. If stream components are chemically active, any time lag between sampling and analysis would cause analytical accuracy and precision to deteriorate. The problem becomes more complex when multi-analytical methods have to be used off-line in order to measure the entire range of stream components. example, ammoxidation For of propylene, a well-known process for making organic nitriles, requires reactor effluents to remain at elevated temperatures (>200°C) [9]. This is to minimize undesirable side reactions such as polymerization of cyanohydrin formed from hydrogen cyanide and water. The challenge of taking samples from such a stream for accurate analysis is obvious. The established method in use [9] has first to obtain a quench sample, which is followed by several laborious analyses in a chemical laboratory. Only a very limited number of determinations can be made per day per

reactor. The long time lag makes it extremely difficult to follow closely and respond rapidly to any reactor condition change. In addition, since the analytical results reflect merely compositions of 'scrubbed' samples instead of reactor effluent in real time, the errors involved in calculating material balances can be large at times. In a commercial plant, a small difference in percentage yield will have significant economic impact.

By using an on-line quadrupole mass spectral analyzer, however, it is possible to analyze olefin ammoxidation streams in real time [10, 11]. The sensitivity, specificity, selectivity, and fast analytical cycle time provided by the process mass spectral analyzer allow process and production engineers to optimize and model reactors in real time at a level previously unattainable. Components normally not analyzed by a gas chromatograph can be routinely monitored by a quadrupole analyzer. Substantial savings can be realized not only through the continuous optimization of feed streams at v ious stages of production, but also through the et er timing of catalyst regeneration cycles neces .ry to refresh catalyst surfaces [12] to maintain o timal vield.

The fact that a quadrupole analyzer can operate in either the full scanning mode or the selected ion detection mode allows timely detection of unexpected by-products from either reactor upset or catalyst changeover. Fast analyzer response time also speeds up reactor modeling studies. Reactor conditions can be changed successively, and corresponding changes in effluent composition can be monitored qualitatively and quantitatively in real time. This greatly facilitates pilot studies essential for evaluating catalyst performances [11].

## FUTURE DEVELOPMENTS

There have been many significant advances in mass spectrometry in recent years that can have an impact on the future development of process mass spectrometry. One of the most important new developments is mass spectrometry/mass spectrometry (MS/MS) [13]. The technique can be implemented by a triple quadrupole mass spectrometer, which can be used as a sophisticated on-line analyzer. The main advantage of MS/MS is its superior capability of focusing the analysis on selected components in an extremely complicated chemical environment. Real time monitoring and measurement of sulfurcontaining gases from pyrolysis of Green River oil shale has been demonstrated recently in the laboratory using a triple quadrupole mass spectrometer [14]. The sulfur gases monitored included hydrogen sulfide (H<sub>2</sub>S), carbon disulfide (CS<sub>2</sub>), carbonyl sulfide (COS), mercaptans (RSH, where  $R = CH_3 -$ ,  $C_2H_5 -$ , and  $C_3H_7-$ ), dimethyl sulfide, dimethyl disulfide, and thiophenes. The measurement of these reactive gases was accomplished on-line in spite of the presence of hundreds of other chemical compounds. This shows that MS/MS has great potential as an on-line analyzer to provide highly selective chemical information difficult to obtain otherwise.

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