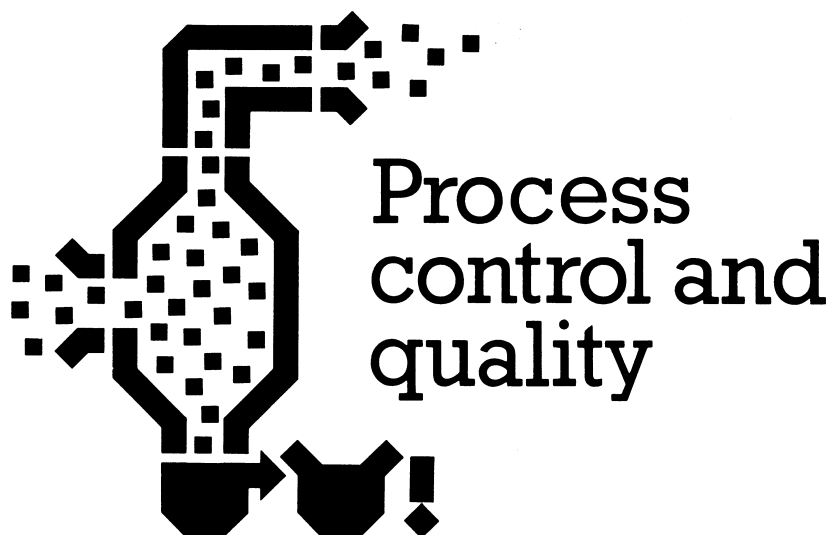# Process control and quality

Application

Permeation tube sources for internal standards in process samples

J.J. McKinley [a,*], Dale C. Merriman [b]

[a] Kin-Tek Laboratories, 504 Laurel Street, La Marque, TX 77568, USA
[b] Mertech, Inc., USA

Process control and quality

The science and technology of process quality measurement systems

An international journal

Aims and scope

In-process analytical instrumentation is becoming increasingly important for process control and product quality measurement in a production environment in many industries, including the following: petroleum, petrochemical, chemical, pharmaceutical, food and biotechnology. The journal provides a multidisciplinary forum for scientists and engineers involved in research, plant design, process quality control and environmental monitoring. Chemists, chemical / mechanical / electrical and instrument engineers, computer scientists, quality assurance engineers, instrument manufacturers and consultants form the primary audience.

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Abstract

Current analytical systems need high-level, on-line validation to assure the accuracy required of them. Adding internal standards to samples provides a system validation reference for each analysis, or as frequently as desired. For concentrations in the ppm and ppb range, permeation tubes are an ideal source for adding internal standards. Adding the standard as near the sample acquisition point as possible will give the most system performance data.

Keywords: Permeation tubes; Internal standards

1. Introduction

Over the last four decades the field of process analysis has evolved rapidly. We have progressed from a few rudimentary techniques, such as the Orsat analysis and thermal conductivity, to an array of complex, highly sensitive instruments which can give essentially real-time process stream composition data. Typically, instrumental analysis methods have been developed in the research laboratory, have progressed to routine use for quality assurance analysis, and ultimately adapted to automated sampling for on-line analysis.

In this evolution there have been two clear trends. One trend is toward monitoring for ever lower concentrations of trace impurities. For example, in olefins production we have pro-

gressed from struggling to measure product distribution at percentage levels to monitoring for low ppb of carbonyl sulfide and other compounds in the product. In the environmental area we now measure low ppb concentrations of toxic organics in ambient air, and in the semiconductor industry process gases are continuously monitored for 0–100 ppb (or lower) moisture.

The other trend is toward ever more complex analytical systems. Multifunctional gas chromatographs have been commonplace for many years.

Continuous sample dilution is now common for emission monitoring systems, and ppb levels of toxic organics are measured by preconcentration plus gas chromatography plus mass spectrometry, and on a field sample collected in a small stainless sphere and transported back to the analyzer.

The combination of trace levels and complex procedures leads to continual doubt about the

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* Corresponding author.

accuracy and precision of the data from these analyses.

We have not adequately addressed the problems of ascertaining accuracy (i.e. calibration) and validating the proper operation of systems between calibrations. The recent trend toward statistical process control further emphasizes the need for continual, routine validation of our analytical data.

2. Current practice

Common practices for assuring analytical data quality are inadequate for dealing with these new challenges. Analytical system performance is typically checked only intermittently, and often infrequently. The validation tests are done with the system off-line.

The calibration standard used is generally totally synthetic, and its overall composition may be quite different from the actual sample, so sample-specific problems may go undetected. An example of a resulting problem occurs in the measurement of trace sulfur compounds in high-purity olefins. Specific compounds are very important, so gas chromatography with sulfur-specific detection is the method generally used. Olefins coeluted with sulfur peaks are not detected, but they will affect the sensitivity of the detector to sulfur compounds. Using a calibration mixture of sulfurs in nitrogen gives an incorrect calibration for sulfurs in olefins, and in fact, the error will be greatest for the lighter sulfurs eluted on the tail of the major olefin peak.

Response linearity is typically established during the method development phase, but often not rechecked as a part of routine evaluation.

Finally, the detection element itself may be the only portion of the system actually calibrated, and the standards used are often of questionable accuracy. In short, current practices do not monitor overall system performance.

The use of internal standards can considerably improve the reliability of complex, high-sensitivity analytical systems. An internal standard is a measurable component of independently known concentration which occurs in each sample. By monitoring this known component along with the unknown analytes we obtain a continual indication of system accuracy and performance. For example, in ambient air analysis, one might monitor the carbon dioxide or argon concentration as an internal standard.

3. Applying surrogate standards

Unfortunately, most process samples have no fixed concentration component which can be used as an internal reference standard. The method can still be applied by continuously adding a fixed concentration of some surrogate compound to the sample, to create an 'acquired internal standard'.

Choosing a suitable compound can be a challenge, however. Ideally, one would want to choose a compound not expected to occur naturally in the sample. When this is not possible, making an intermittent standard addition is an alternative. The surrogate should have similar structure, vapor pressure, and polarity as the key analyte, and the concentration added should be in the same range. Of course, it is essential that the surrogate be compatible with the detection method, and not interfere with the analysis. Examples of suitable surrogates include the addition of hexachlorobenzene in ambient air samples being monitored for halogenated aromatics. Or, when mass spectrometry is the detection method, the deuterated analog of an analyte may be used.

The key to implementing the 'acquired internal standard' method is finding a suitable source for the surrogate compound. Ideally the pure compound should be added directly to the sample stream. If a prediluted source is used, the diluent volume becomes a significant factor in the analysis, and the actual result may be a
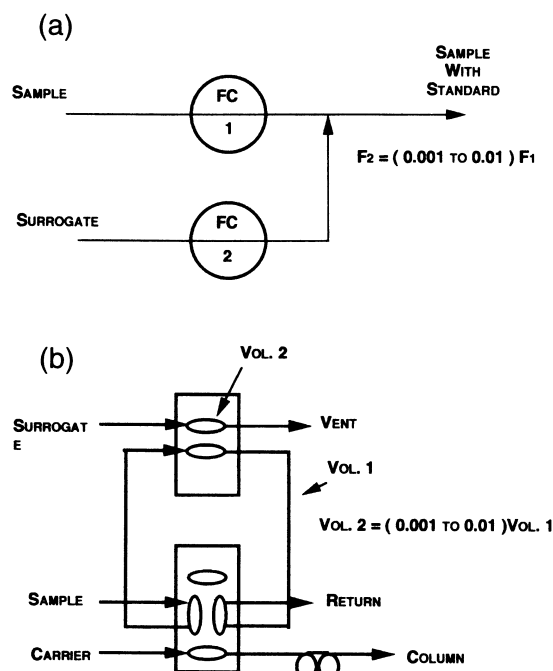
(a)

(b)

Fig. 1. (a) Direct blending method. (b) Volume ratio method.

decrease in data quality rather than an improvement.

For concentrations in the 0.1–1% range, simple direct injection from a compressed gas cylinder is possible. Fig. 1a shows a flow diagram of such a scheme. For discrete sampling analyzers, Parks and Hinkle [1] have described a volume ratio technique which can frequently be

used in this concentration range. A schematic of this method is shown in Fig. 1b.

When the concentration level needed is in the ppm or ppb range, however, the situation is much more complex. For example, to make a 1 ppm mixture 1 ml/min of surrogate must be added to 1000 1/min. Flow control at 1 ml/min and below is itself an onerous problem, and 1000 1/min sample flow-rates are not practical.

When the surrogate compound is a liquid, vaporizing it into the sample stream can be a very difficult application problem.

Using permeation tubes as the source for the surrogate compound avoids the problems described above. A permeation tube is a device which uses the permeation of vapors through a polymeric membrane as a very stable, very low gas flow source. In use, the pure compound is on one side of the membrane and the sample flows over the other side. Flow-rates through the membrane can range from a few nanoliters of vapor per minute to over one milliliter per minute. The pure surrogate can be either liquid, gas, or a subliming solid.

4. Permeation tube operation

Fig. 2 shows a basic permeation tube. A supply of the surrogate compound (in this case a
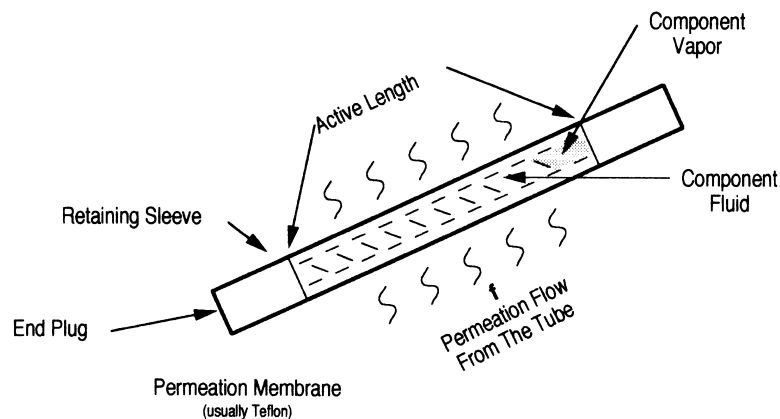

Fig. 2. Basic permeation tube.

liquid or liquefied gas) is sealed inside a length of polymeric (usually Teflon®) tubing. Surrogate compound vapor flows out through the tubing walls at a rate f, where

$$f = K(T)\frac{KA\Delta P}{t} \qquad (1)$$

In this equation, f is in nanogram per minute, K is the permeability characteristic of the membrane–surrogate compound combination and is a function of the membrane temperature, A is the area of the membrane, i.e. the tube wall area, and t is membrane (tube wall) thickness.

ΔP is the difference in partial pressure of the surrogate vapor across the membrane, where

$$\Delta P = VP_{\text{inside}} - VP_{\text{outside}} \qquad (2)$$

The pressure inside the permeation tube is merely the vapor pressure (VP) of the liquid surrogate. Since we are dealing with very low concentrations, the vapor pressure outside the tube is effectively zero. So, for practical purposes, ΔP becomes just the surrogate pressure in the tube.

The permeability characteristic K is given by

$$K = K_0 \exp(b/T) \qquad (3)$$

where K_0 and b are constants, and T is the absolute temperature in K.

In Eqs. 1–3, all the variables except the temperature and the pressure of surrogate compounds vapor are fixed when the tube is made.

The emission rate of the surrogate (f) can be measured by holding the tube at a constant temperature and weighing it periodically to determine the rate of weight loss. Thus,
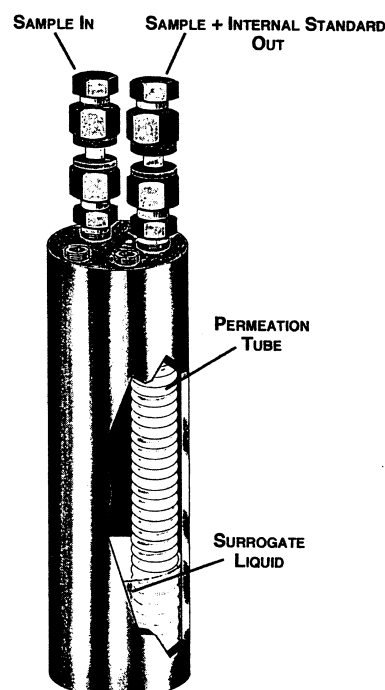
$$f = \frac{W_i - W_f}{t_i - t_f} \qquad (4)$$

Fig. 4. High-emission permeation tube.

where W_i is the initial weight of the tube, W_f is the final weight and $t_i - t_f$ is the elapsed time between weighings.

Since the factors controlling the emission flow (temperature and pressure) are fundamental properties, permeation tubes are actually primary standards.

To generate a fixed concentration mixture, the tube is immersed in a known flow of dilution gas (see Fig. 3). For creating an acquired internal standard, the sample stream would be the dilution gas. Several tubes can be placed in the sample simultaneously to add multiple components if required.

By changing the dimensions and design, the tubes can be applied to a wide range of com-
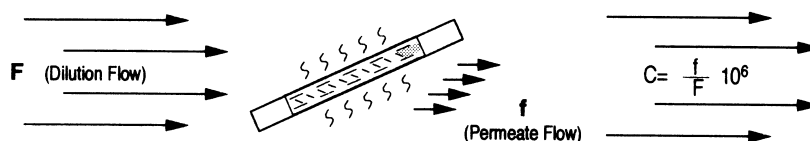

Fig. 3. Use of permeation tubes.

pounds and made to cover a broad range of emission rates. Tubes are commercially available for over 300 compounds.

A particularly useful design is the inside-out configuration. Fig. 4 shows a design in which a long coil of permeation tubing is immersed in a stainless steel canister containing the surrogate compound. Dilution gas flows concentrically through the tube instead of around it. This design allows access to the surrogate compound without breaking the membrane seal, so the tube is refillable. It can also be used for gaseous surrogates, but in this case the surrogate pressure must be mechanically controlled.

Permeation tubes have a very wide applicability. They can be used for virtually all reasonably stable compounds from atmospheric gases to organics with boiling points in excess of 200°C, and can give concentrations typically from about 1 ppb in 5 l/min to over 100 ppm in a l/min.

5. Application details

Systems using permeation tubes to add the surrogate compound can be quite simple. All that is required is that the sample flow be controlled (or at least carefully measured), and that the permeation tube temperature be held constant. Fig. 5 shows a typical system. Here, a bypass feature has been added to allow dynamic testing (i.e., to show the speed with which the system will respond to changes in concentration).

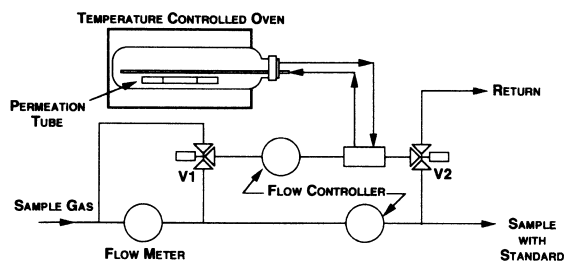In this apparatus, the permeation tube is in a

Fig. 5. Flow diagram standards addition system.

bypass loop of the sample line. When the standard is being added, the metered sample flow is divided. A small portion flows over the permeation tube, mixes with the permeated surrogate, and returns to the main sample flow. This produces a sample with an acquired internal standard.

Actuating valves V_1 and V_2 isolates the permeation tube from the main sample stream, but keeps fresh sample flowing over it. This feature has two functions. It produces a step change in sample composition which can be used for diagnostic purposes. Observing the detection system response when the surrogate is switched on or off gives an estimate of the true response time of the system. Problems such as adsorption in sample lines or sample conditioning elements are clearly indicated. It is entirely possible for a sample system with a 2-min residence time to have a 5-h response time!

This design also allows system validation by 'standard addition' to a component normally present in the sample. For example, in moisture analysis, using a surrogate compound is usually not an option. But a known amount of water can be added to the sample periodically to demonstrate proper system operation.

Note also in Fig. 5 that several permeation tube ovens could be installed simultaneously if multiple components are needed.

The internal standard should check as much of the system as practical. If possible it should be added right at the sample acquisition point, so that the entire analytical system is checked. When that is not possible, introduce it as far upstream of the detector as practical.

Fig. 6A–F shows simulated bar chart responses from using the system shown in Fig. 5. Fig. 6A shows response to a normally operating system. The slight variations indicate overall system precision. Note also the drift in response due to changes in atmospheric pressure. Ratioing response to analytes to that of the internal standard cancels many of the errors introduced by unmeasured factors and substantially increases overall accuracy.
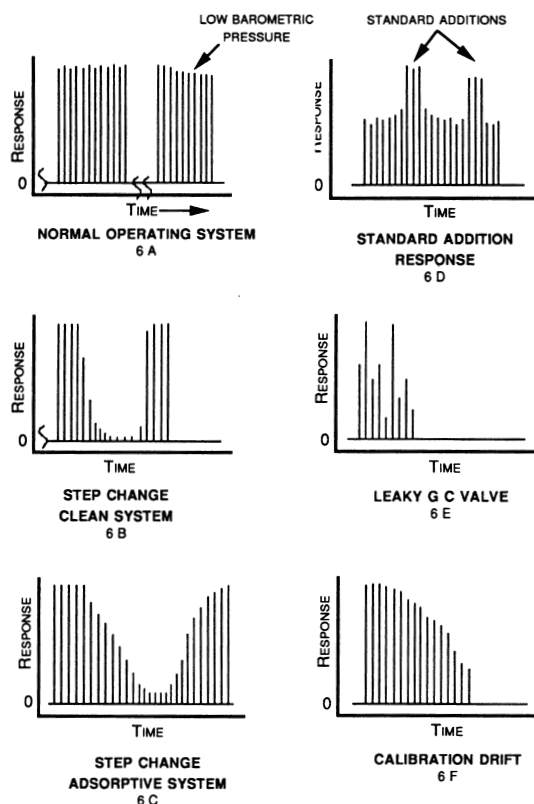
Fig. 6. Simulated response to internal standard.

Fig. 6B and C show response to step changes in the internal standard for a clean, responsive system and an adsorptive one. Note the rapid drop to zero in B vs. the slow decline in C. Changes in analyte concentration are measured with similar response time.

Response to standard additions is shown in Fig. 6D. Effective use of this technique on-line requires some computational capability in the system. The system must be able to measure the difference in response due to the addition of the standard, and interpret changes in that response in relation to changes in background concentration in the sample gas.

Fig. 6E and F show typical responses to fault conditions. In Fig. 6E, a GC sample valve has developed a leak. As is typical, response is lower and unsteady [1], since the amount of sample lost varies during each actuation. In Fig. 6F the system is simply losing sensitivity.

Other fault conditions will produce similar typical responses which can be used for diagnostic purposes. In current systems there is usually no early indication of a fault. Faults are discovered during periodic routine calibration, or when the data is obviously erroneous.

References

[1] J.C. Parks and E.A. Hinkle, A New Calibration Method for Process Chromatography, pp. 217–220.

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