

Testing at the limits

Calibrating and validating ppm and ppb on-line analysers



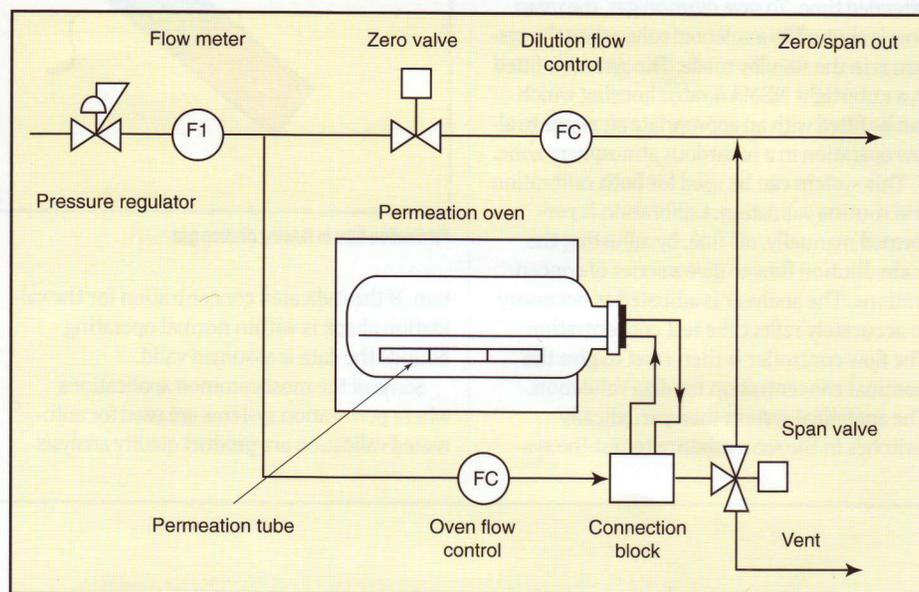
The Span Pac I

On-line analytical measurements have become commonplace in the petrochemical and other processing industries. Operators rely heavily on this up-to-the-minute analytical data for guidance in making the day-to-day operating decisions. Often, analysers are actually in closed loop control of some portions of the process.

But despite heavy reliance on data from these analysers they often receive much less attention than their laboratory counterparts.

When the analysis is for product quality monitoring or personnel safety assurance the concentrations measured are often in the ppb to low ppm levels. At these trace concentrations analytical systems (including sample acquisition, transmission, conditioning, analyte measurement and data analysis) tend to be less robust. At low concentrations there are fewer analyte molecules in the sample. So, loss of analyte to active surfaces or micro-contamination in the system becomes very significant and may result in drift or non-linearity. In short, they need frequent checks to validate the accuracy of the data generated.

To insure reliability, careful, multi-point calibration and frequent data quality validation is required. The traditional source for gas standards for this function has been static



Basic Flow Diagram

blends supplied in high-pressure cylinders. At higher concentrations that method is very convenient and relatively low in cost. At lower concentrations it is much less useful. Mixture stability is the problem. Reactive and polar molecules interact with the cylinder walls causing the analyte concentration to continually decrease. Also, if any of the analytes react, they must be supplied in separate standards. When the mixture must be in the sample matrix, it can be very difficult to obtain a source of the matrix gas that does not already contain traces of the analytes, thus making it difficult to establish the true concentration of the mixture. In the end, performance of the system may be limited by the quality of the gas standards used for calibration.

The problems noted above can be avoided and reliable, accurate standards obtained by dynamically blending the mixtures *in situ* using permeation tubes as the analyte source. A permeation tube is a device that uses the flow of vapour through a permeable membrane to create a very small, very stable flow of analyte vapour.

A typical permeation tube is made up of a short length of Teflon tubing with a supply of pure analyte liquid sealed inside. The analyte vapour flows through the tubing wall. Holding the tube at constant temperature produces a very steady, very small, and very re-

producible flow of analyte vapour. This flow can be measured by weighing the tube periodically and observing the rate of weight loss. Mixing this flow with a much larger, known flow of dilution gas creates a flowing standard of known concentration. This technique allows single step dilutions of up to 10⁹:1, so you can make a 1ppb mixture directly from the pure analyte.

Several permeation tubes can be combined in the same container and simultaneously mixed with the dilution gas to form a multi-component mixture. A range of concentrations is obtained by varying the dilution flow. By maintaining traceability of operating temperature, rate of weight loss, and dilution flow to national standards, the resulting mixture concentration becomes traceable through those physical standards. Traceability is not available for most ppm and ppb static mixtures.

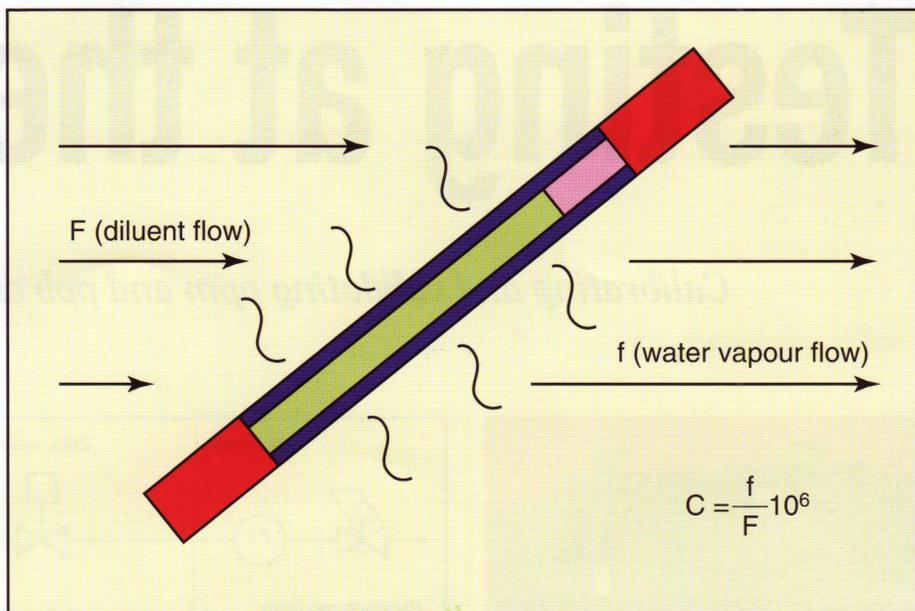
While the permeation tube method is commonly used in the laboratory, it has not been widely used with on-line analysers. Most instruments for using permeation tubes are not designed for easy adaptation to field use. The Span Pac I Industrial Series are an exception. These systems use a simple flow path that is designed for ease of automation.

In the Span Pac I system the entire dilu-

tion flow is measured with a single flow meter. Downstream of the meter the flow divides into two parts. A small portion passes over the permeation tube(s) and acts as carrier for the permeate. This flow is continuous and can be either mixed with the main dilution flow to form span gas mixture or switched to vent so the main flow becomes 'zero gas.' The main dilution gas flow is adjusted to obtain the desired concentration for the span gas.

Both flows are controlled by flow controllers which automatically compensate for changes in back pressure to hold a steady flow over an extended time. To save dilution gas, the main flow is shut off by a solenoid valve when the system is in the standby mode. The system is fitted in a watertight NEMA 4 rated housing which can be fitted with an appropriate air purge to allow operation in a hazardous atmosphere zone.

This system can be used for both calibration and routine validation. Calibration is performed manually, off-line, by adjusting the main dilution flow to give a series of concentrations. The analyser is adjusted as necessary to accurately reflect the test concentration. The flow controller is then reset to give the nominal concentration for data validation. The analytical system then periodically switches in the span mixture to test the sys-



Permeation tube in flowing dilution gas

tem. If the indicated concentration for the validation check is within normal operating bounds the data is assumed valid.

Some of the most common applications where permeation systems are used for automated validation are product quality analysis

for polymerisation grade ethylene and propylene, fence line monitoring applications around petrochemical plants, pipeline monitoring to assure delivery of high quality feed gases.

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