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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Bruno, Thomas J.(2005) 'Conditioning of Flowing Multiphase Samples for Chemical Analysis', Separation Science and Technology, 40: 8, 1721 — 1732
To link to this Article: DOI: 10.1081/SS-200059616
URL: http://dx.doi.org/10.1081/SS-200059616

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Separation Science and Technology, 40: 1721–1732, 2005
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200059616

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Conditioning of Flowing Multiphase Samples for Chemical Analysis

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Abstract: The chemical analysis of process streams is a common task that must be completed thousands of times every day in the chemical industry. In refineries, at gas wells, in chemical processing plants, and in fine pharmaceutical facilities, there is a continual need for the chemical analysis of products and intermediates. Less common but no less important are the many instances in which such process samples must be handled in state-of-the-art analytical chemistry labs. Unlike the typical samples presented in the analytical laboratory, process streams are seldom well behaved. Very often, process streams present multiphase samples to the analytical device. In this context, multiphase means that there is a gaseous or vapor phase plus one or more liquid phases. Because of the complexities of vapor/liquid equilibrium, a multiphase (two or more phase) mixture cannot be analyzed reliably. Sample conditioning is required before any analysis is attempted. This means that the gaseous and liquid fractions of the sample are separated into two distinct regions or streams. Moreover, the two phases must be retained in the device with complete integrity. That is, they must not be changed in any way by the separation device. In this paper, a simple approach to conditioning such multiphase samples is described. This approach permits the reliable analysis of each phase.

Keywords: Chemical analysis, separator, two-phase flow

Received 15 August 2004, Accepted 31 January 2005

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INTRODUCTION

Chemical analysis, broadly defined, consists of measuring the identity of components and the composition (relative quantity of each component) for a given sample. Samples are presented for analysis in a variety of different ways, some more facile than others. For example, samples that are presented for analysis as a multiphase mixture flowing in a pipe or transfer line are a particularly challenging problem. In this context, multiphase refers to a vapor or gas phase that is mixed with one or more liquid phases, usually, but not always, in an equilibrium state. If one desires to analyze the vapor phase of the mixture, it is critical that the vapor be physically separated from the liquid. If the vapor sample is contaminated with even a small quantity of the liquid, the analytical result will be erroneous, often seriously so. The same reasoning applies if one desires an analysis of the liquid. In fact, it is common that both the vapor and the liquid phases of a two-phase mixture must be separately analyzed, while retaining the full integrity of both phases.

An Illustrative Example

On a large and dramatic scale, an example of a chemical analysis applied to a two-phase flow may be found in the natural gas industry. Natural gas is a complex, multiphase mixture consisting of upwards of 200 components, most of which are naturally occurring (1–6). The gas phase consists primarily of methane and some of the lower hydrocarbons such as ethane and propane. In addition to this gas phase, however, there is a coexisting liquid phase consisting of higher hydrocarbons and treatment compounds. These are collectively termed natural gas liquids. As the gas is transported through pipelines, the natural gas liquids also flow along with the gas. These pipelines are typically very large, and can be up to 36 inches in diameter. Some operate at pressures approaching 8.3 MPa (1200 psig), and temperatures that run from 100°C (at a compressor outlet) to −20°C in traversing colder regions. Under the influence of these variables, the multiphase behavior is quite complex. There are four flow regimes that can describe the action of the liquid in the pipeline (7). They are presented here because they are relevant to any instance of two-phase flow:

Stratified flow—a flow regime in which the liquid layer travels smoothly (with little or no disturbance of the liquid surface, such as waves or ripples) along the bottom of a pipeline or transfer line, under the influence of the motion of the gas or vapor traveling above the liquid. This regime is observed at the lowest gas or vapor velocities.

Wave flow—a flow regime that occurs at gas velocities somewhat higher than that of stratified flow, in which the smooth surface of the liquid is disturbed by a wave pattern set up by the influence of the more rapidly moving gas or vapor.

Annular flow—a flow regime that occurs at high gas velocities, in which the liquid flow takes place along the entire inside periphery of the pipe, or along the annulus of the pipe, under the influence of the flowing gas or vapor. In this case, the liquid forms a coating on the inside wall of the entire pipe.

For the three regimes discussed above, the crossover from one regime to another is gradual, and is based upon a number of factors including liquid level, liquid density, liquid viscosity, pipe geometry, and gas velocity. For this reason, it is not possible or advisable to be more exact when specifying the velocity, other than by the use of the relative terms identified above. The other flow regime, which does not fit neatly into the above scheme, is slug flow:

Slug flow—a flow regime in which relatively large volume elements of liquid (called slugs) that entirely fill the pipe are pushed along by the gas or vapor flow. Typical slugs are between 5 and 1000 pipe diameters in length.

The occurrence of slug flow is a result of relatively high liquid volume, and changes in gas velocity. Typically, slug flow will occur when liquid that has accumulated in a low point is suddenly accelerated by an increased gas velocity. In the natural gas example, this can occur at the initial onset of cold weather, when the demand for natural gas jumps after a sustained period of lower usage.

For many reasons, the composition of natural gas must be measured at points along the transmission pipeline. These reasons include quality control, calorific value determination, and system maintenance. In the analysis of the gaseous fraction of a flowing natural gas pipeline, one must take measures to ensure that liquid is not permitted to enter the analytical device. Similarly, a chemical analysis of this phase is also often required, since the natural gas liquids are considered a pipeline asset. In this case, it is important that the liquid composition not be compromised by the presence of gas. Moreover, one must be able to sample when the line is flowing in stratified, wave, annular, or slug flow. It is critical for the analyses that each phase retains its integrity prior to chemical analysis. By this is meant that the protocol of gas/liquid separation cannot alter the composition of either phase under the sampling conditions.

This example serves to illustrate the complexities of sampling two-phase fluids from flowing streams. The presence of some vapor contribution from the natural gas liquids is a natural consequence of the thermodynamics of phase equilibrium. These constituents *must* be present in the vapor to give the analysis a true representation of the vapor composition. The only requirement is that volume elements of liquid (at the sampling conditions) be excluded.

We now shift the discussion from this macroscopic example to the very much smaller sizes encountered in laboratory work. In the analytical lab, and with on-line, in-line, and at-line analyzers on industrial processes, many of the same types of problems occur. They can be more vexing, however, because instead of dealing with a ≈ 1 m (36-inch) cross section of pipe, one typically must face the same difficulties inside of a length of capillary tube. The analyst will commonly have to analyze the gaseous component of a flowing multiphase mixture inside a tube having an internal diameter of 0.5 mm (0.02 inch) or less.

Analytical laboratory examples of flowing multiphase samples occur in industrial and research labs every day. The only labs that might not have to handle such samples on a regular basis are perhaps undergraduate teaching labs. One can cite numerous examples in which the analytical sample is presented as a flowing multiphase mixture, such as:

- pressurized fuel gas samples;
- supercritical fluid extractant streams;
- fermentation broth samples;
- polymer and chemical process headspace samples;
- food product quality control samples and process probes;
- abandoned mixed waste drum sample lines.

Previous Gas Liquid Separators

Because of the long history (extending back nearly a century) of gas-liquid separators, some discussion is warranted before any new device is introduced. In the vast majority of these reports, the devices are designed to condition the flow of rather large volumes of two-phase streams, typically with a knock-out tank (8). A knock-out tank is simply a large volume in which the flow rate is allowed to decrease. Other designs of gas-liquid separators employ a mantle structure to slow and coalesce the liquid phase. Devices that use this approach are sometimes called demisters. The mantle of a demister can be a honeycomb structure, a structured packing, or simply an interactive paper, fiber or polymeric pad, mat or cartridge. The presence of these structures as part of the gas liquid separator makes the devices unsuitable for application to chemical analyses. Such structures are by their nature adsorptive, will invariably interact to a significant extent with the sample, and change the composition of either the gas or liquid phases. Other commercial gas-liquid separators employ a bed of glass beads (also an adsorptive site) as a coalescence medium.

The most common of these are used in inductively coupled plasma (ICP) and flame/furnace atomic absorption spectroscopic (AAS) techniques (9–19).

Typically, these devices are constructed of glass, which limits the pressure at which an analytical scale device may be operated. In addition, most of these devices require an additional, separate purge or reactant line in order for them to function. This is acceptable in ICP and AAS, where, for example, an argon purge or an acidic reactant gas might be necessary to convey sample to the flame or plasma. In general sampling applications, when one simply desires to split the vapor and liquid flows for subsequent chemical analysis by any method of the operator's choosing, such a purge will not be acceptable because it will change the sample.

Another important aspect of most of these existing separators is that the liquid that is separated is generally considered and treated as a waste stream, the integrity of which is unimportant. This is also the approach with the membrane separators described above as interfaces for mass spectrometers and other analytical devices. Moreover, the beds or frits used for coalescence are difficult to clean between samples. This is unimportant when the liquid stream is considered a waste and discarded. If one desired, however, to recover the liquid for subsequent analysis or use, this type of separator would not be optimal. Moreover, the glass beads and sintered frits are adsorptive and reactive (as Lewis acids) unless they are treated. In addition, these separators often require the presence of a liquid phase in order to function at all. Thus, the separator must operate for a certain amount of time before it begins to remove the liquid efficiently. Such devices are clearly not suitable for use with small analytical samples, since allowing the separator to function for a "seasoning" period will deplete the sample, and the sample composition will change with time.

Another common gas-liquid separator employs a cyclone generator or swirl tube to separate the liquid phase, or a liquid suspension of solids (20–22). Again, the application of this component is inconsistent with the goals of chemical analysis, for two primary reasons. First, the cyclone has a tendency to generate foam in the collected liquid phase. This will complicate the analyses of both phases because the foam will have a surface area higher than that of the original liquid phase. The partitioning of components between phases can be changed by this. Second, the cyclone is a relatively large component relative to the pipe or tube diameter. This can make recovery and subsequent analysis of the liquid phase a more difficult problem.

Polymeric membranes are occasionally mentioned as gas liquid separators (23–26) and as sampling accessories (27–29). These are to be distinguished from the polymeric mantles discussed above in that the polymeric membrane forms a barrier, not simply a surface, to achieve the separation. Usually, the membrane is designed to separate only specific components present as a liquid. Typically, this component is water, and in such cases, the approach can be very successful. As an example, one may consider membrane interfaces mentioned earlier for mass spectrometers, which have been very useful in removing the analytes from well-defined matrices that are present in very large excess (i.e., the solvent). In general, the separation by a membrane is governed by the solubility and diffusivity of components in the membrane. For this reason, the membrane cannot help but partition components, and will not provide a true gas liquid separation in the sense of an arbitrary analyte stream. Membrane devices are therefore often unsuitable for general use as gas-liquid separators in chemical analysis.

EXPERIMENTAL

Recently, NASA required the characterization of the thermal stress products of a kerosene-based rocket propellant called RP-1 (30). This work was done using an ampoule approach to reaction kinetics that was developed at NIST (31). In this technique, depicted schematically in Fig. 1, one places a weighed quantity of RP-1 in a high-pressure ampoule having a known volume. The ampoule, constructed from thick-walled 316L stainless steel tubing, is then sealed with a high-pressure valve. The ampoule is evacuated through the valve to remove air, and then it is placed in a thermostatic block at the desired temperature. Exposures at temperatures between 375° to 500°C for periods ranging from 15 to 200 minutes produce a high-pressure two-phase mixture that subsequently must be chemically analyzed. Simply opening the valve to the ampoule will allow the reacted fuel to spew out of the ampoule as a multiphase "soup," thus making it impossible to separately analyze the vapor and liquid phases.

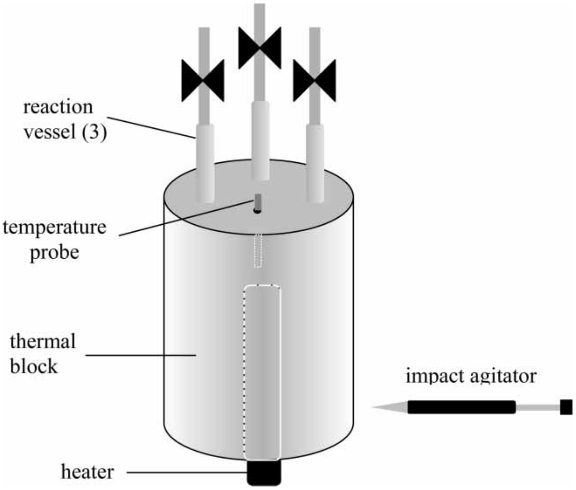

Figure 1. A schematic diagram of the ampoule testing apparatus used at NIST to study thermal stresses in fluids. It consists of a heated stainless steel block that holds multiple sample cells. An impact agitator is provided for mixing, when a heterogeneous catalyst is added to the samples.

Since a chemical analysis of the vapor and liquid phases of the reacted fuel was necessary, some reliable means of separating the liquid from the vapor, while preserving the integrity of both phases, was needed. To achieve this, the device shown in Fig. 2 was designed and constructed. This device, which is similar in concept to branch point separators in natural gas transmission lines (32), is constructed from a 316 stainless steel tube "tee" fitting. Branch point separators have demonstrated effectiveness due to the increase in volume of the enclosure and the position of the vapor collection tube. The branch on the left-hand side of the figure consists of a 6.4 mm (1/4 in) outside diameter (o.d.) section of stainless tube into which a 1.6 mm (1/16-in) o.d. tube has been brazed. This length of 1.6 mm o.d. tubing has an inside diameter of 0.5 mm (0.020 in). A conical shape is machined into the end of the 6.4 mm tube, cutting back the 1.6 mm o.d. tube by a few mm. This branch of the device comprises the flowing multiphase sample entry line.

The branch on the right-hand side consists of a section of 6.4 mm o.d. 316 stainless steel tube into which a length of 1.6 mm o.d. tube has been brazed. The inside diameter of this section of this 1.6 mm tube is also 0.5 mm. The terminal end of this length of this tube is sealed with a brazed plug. On the top of this length of this tube, approximately 1 mm from the sealed end of the tube, a hole is drilled into the circumference of the tube. This hole has a diameter of 0.5 mm (0.020 in). This branch comprises the vapor outlet of the device.

The bottom branch of the "tee" consists of a stainless steel cap, and is used as the liquid collection area. The cap can be replaced by a liquid collection vessel of any size that is desirable, consistent with the size of the liquid

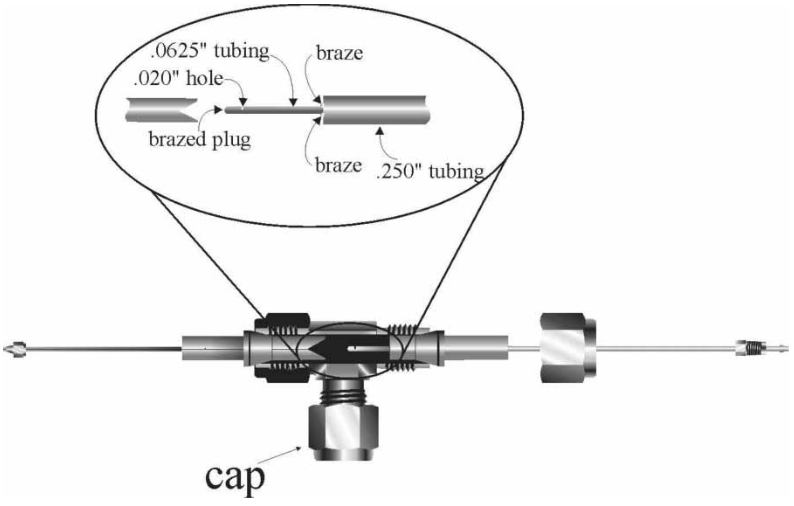

Figure 2. A schematic diagram of the gas-liquid separator used in this work.

fraction of the sample. The operating configuration of the device is as it is shown in the figure. That is, the cap must be positioned on the bottom of the separator for the device to function.

The device as described above can safely operate at 35 MPa (5000 psig). The maximum operating temperature of the device is approximately 600°C, although the allowable pressure at ambient temperature must be de-rated proportionately at higher temperatures (above 250°C). In all of the work that will be discussed here, the conditioner was operated at ambient temperature. Operation at higher temperatures might be desirable for highly viscous samples or to mimic conditions in the source reactor. Some control of the sample pressure in the conditioner can be affected by simply controlling the flow rate from the source reactor, although more sophisticated approaches can be envisioned.

Before operation, and periodically throughout its useful lifetime, the device is passivated with an acid mixture and washed thoroughly. As an alternative for use with particularly reactive or adsorptive samples, the components may be treated to produce a surface of fused silica (33, 34).

To operate the device, the source of the multiphase flowing sample is connected to the left-hand branch. The flowing multiphase sample is then routed to the device, usually by a valve. As the multiphase stream enters the “tee”, the velocity of the fluid will decrease because of the increase in volume that the fluid encounters upon entering the “tee”. The mass flow rate will be undiminished because gas will exit the hole drilled in the top of the tube brazed into the right-hand branch. If the velocity of the sample places the flow in the stratified or wave-flow regime, the liquid fraction will simply drop into the collection space provided by the cap of the bottom branch of the “tee”. If the velocity is higher, and the flow is in the annular regime, then the liquid flow will continue along the inside periphery of the “tee”, and then be ultimately routed by the interior walls of the “tee” into the bottom branch into the collection cup. In either case, the positioning of the branch on the right-hand side enables the collection of a sample consisting only of vapor. The liquid fraction will be stripped from the flow. On a large and dramatic scale, the visualization of the flow patterns in a conceptually similar device can be observed in the film by Andriessen (32).

It is important to point out that the application of this device does not provide a composition measurement under the temperature and pressure conditions of the ampoule. This device cannot (and is not intended to) replace the measurement of vapor-liquid equilibrium, when such a measurement is called for. Rather, this device is analogous to a gas-tight syringe that is used for chromatographic headspace sampling. Note that if such a syringe were to become contaminated with the liquid (below the headspace), the analysis would be erroneous. Thus, with this device, the temperature and pressure conditions that apply are those of the conditioner itself, which the operator can specify to some extent (with temperature and flow rate).

RESULTS

The application of the sample conditioner as described in this paper has enabled completion of the analysis of the vapor and liquid fractions of thermally stressed RP-1 rocket propellant. The valve of the ampoule (Fig. 1) was connected to the left-hand branch of the conditioner. The outlet on the right-hand side of the conditioner (the sample outlet) was connected to a length of fused silica capillary tubing (530 μm inside diameter, with a polyimide coating on the outside). When the valve to the ampoule was opened, a gaseous sample, with the liquid stripped away, was available for analysis. This flow was analyzed by simply inserting the fused silica capillary (with the gaseous sample flowing out) into the septum of a split-splitless injector of a GC-MS-IR instrument. The total ion chromatogram (from the MS) and total response chromatogram (from the IR) of the gas phase were then recorded. Upon completion of the vapor analysis, the cap forming the bottom branch of the conditioner was opened, and the liquid sample was recovered from the well. The liquid was subsequently analyzed by dissolving the liquid in an appropriate solvent, followed by syringe injection into the split-splitless injector of the GC-MS-IR. The results of the vapor phase analysis for RP-1 thermally stressed for 66 minutes at 450°C, are presented in Table 1. We do not present an analysis of the results of the recovered liquid here because the sampling of this phase is straightforward, and these results are presented elsewhere (35). In general terms, however, the liquid phase consisted of approximately 300 components ranging in relative molecular mass from 140 to 200. While some of the vapor phase constituents (listed in Table 1) were (not surprisingly) found in the liquid, the concentrations were very different. It is clear that the analyses of both phases, separately, could not have been achieved without the conditioning device.

Table 1. A summary of RP-1 reaction products found in the vapor phase after thermal stress at 450°C for 66 min

Compound name	Mass percent
Propane	46.7
2-Methyl butane	24.9
2-Methyl pentane	7.8
n-Hexane	7.7
Methyl cyclopentane	3.4
Benzene	3.7
1,3-Dimethyl cyclopentane	1.4
n-Heptane	1.8
Methyl cyclohexane	1.4
Toluene	1.2

CONCLUSIONS

A new approach to gas-liquid separation of flowing, two-phase analytical streams has been presented. The device is conceptually simple, and similar to gas-liquid separators used in natural gas transmission lines. We have applied this device to the analysis of a pressurized, two-phase stream of thermally stressed rocket propellant. The device allowed the analysis of the separate vapor phase of this sample in a facile manner. In the future, we will test and apply modifications of the device that will include a vacuum line, so that air-sensitive mixtures can be analyzed.

ACKNOWLEDGMENTS

The financial support of the National Aeronautics and Space Administration, contract *C31053A*, is gratefully acknowledged. The assistance of Dr. Peter C. Andersen, a postdoctoral associate at NIST, is gratefully acknowledged.

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