A compact, lightweight gas standards generator for permeation tubes

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A lightweight, compact gas standards generator for permeation tubes is described. This system provides reliable temperature control during periods of intermittent power and is ideal for field measurements. A eutectic alloy with a high heat of fusion is used as a phase change material. This thermal source allows the system to maintain a constant permeation tube temperature of 46.6 °C for over 5 h in the absence of external power. This permeation system is currently being used in an aircraft chemical ionization mass spectrometer to provide HNO_3 calibration. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1570949]

I. INTRODUCTION

Permeation tubes and permeators are used as standards in a broad variety of applications. Permeation tubes provide a simple method for preparing low concentration gas mixtures, often at the part per million or part per billion level.[1–3] Currently, permeation tubes are produced commercially for more than 400 compounds.

Permeation tubes typically consist of tetrafluoroethylene (TFE) or fluorinated ethylene propylene (FEP) Teflon, which are chosen for their durability and low reactivity. The volatile liquid is sealed inside the cylinder and its gas permeates out. The permeation process consists of dissolution of the vapor into the polymer, diffusion through the polymer wall, and mixing outside of the tube. The difference in partial pressure between the inner and outer walls is the driving force for the process. In theory, the dissolution of gas into the polymer is governed by Henry's law of solubility, while Fick's law of diffusion can be used to describe the flux of gas through the tube wall.[3] Since both of these processes are dependent on temperature, the total permeation rate is also highly sensitive to temperature. A common rule of thumb suggests that each 1 °C increase in operating temperature results in a 10% change in the permeation rate.[3] Equilibration time following a temperature perturbation may vary from minutes to days, depending on the gas, polymer wall thickness, and polymer material.[4]

Maintaining constant temperature is critical during field campaigns when permeation tubes are used as a primary standard. Aircraft measurements present a special challenge where loss of power over minutes to hours occurs during fueling and other processes. Many permeation systems regulate temperature by heating a large thermal mass. Unfortunately, this method has disadvantages of both size and weight. This article presents an alternative system for temperature and flow control which is compact, lightweight, and has good thermal stability.

II. INSTRUMENTATION

A. Temperature regulation

Since permeation rate depends directly on temperature, control of this variable is critical to the system. We sought to maintain a fixed temperature above expected ambient temperatures, in the range 35–50 °C. A phase change material is ideal for this application. Phase change materials have high latent heats of fusion, with corresponding thermal inertia at the liquid-solid transition temperature. Several types of phase change materials are marketed commercially, including eutectic alloys, noneutectic alloys, hydrated inorganic salts, and waxes. We tested both hydrated inorganic salts and a eutectic alloy as possible thermal sources.

Two hydrated inorganic salts, calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) and disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), have reported melting points of 27.45–30.05 and 38–41.5 °C, respectively.[5] When tested in our lab, these salts solidified inhomogeneously, despite the addition of a nucleating agent. In the case of $CaCl_2 \cdot 6H_2O$, the liquid cooled to 24 °C before crystallization began at 27 °C. In a recent study, Liu and Chung concluded that $CaCl_2 \cdot 6H_2O$ and sodium sulfate decahydrate

$(NaSO_2 \cdot 10H_2O)$ were unsuitable for use as thermal interface materials, with or without nucleating additives, due to their incongruent melting and decomposition behavior, large supercooling, and thermal cycling instability.[6] For these reasons, a eutectic alloy was selected as the superior phase change material for our system.

Eutectics are metal alloys with a single melting point, typically lower than the melting points of their constituent metals. These alloys usually consist of a mixture of bismuth, lead, tin, cadmium, and indium in fixed proportions. Currently, eutectics are available with a range of melting points. The lowest reported is 47.2 °C. These materials are marketed for molds and low temperature solders. They are useful in permeation rate regulation as a result of their high heats of fusion. If the eutectic material is melted and held at a temperature slightly above its melting point, it will maintain a constant temperature over several hours after the heat source is disconnected, providing a reliable thermal source during intermittent loss of power. Eutectics are also appropriate because they have high thermal conductivity in both the liquid and solid phases, and experience little expansion upon melting.

In this system, an alloy composed of 44.7% bismuth, 22.6% lead, 8.3% tin, 5.3% cadmium, and 19.1% indium was used. This material is marketed under the name Cerrolow-117 and has a discrete melting point. Although the melting point is generally reported as 47.2 °C,[7] slight variations in composition and metal purity can affect this value.[8] The melting point of our Cerrolow-117 (purchased from McMaster–Carr) was measured as 46.6 °C, using a calibrated platinum RTD. The latent heat of fusion is reported as 1.4×10^4 J kg^{-1}, with a volume difference of less than 0.1% between liquid and solid states.[8]

To assemble the system, Cerrolow-117 alloy is melted and poured into a 8.5 in. long by 1.25 in. diam copper cylinder sealed at one end. A glass *u*-tube containing the permeation tube is inserted into the molten alloy. One arm of the *u*-tube is metal, for increased conduction and heating of the incoming carrier gas. The permeation tube is contained in the glass arm of the *u*-tube. All downstream surfaces are glass or Teflon, to minimize wall interactions with the nitric acid. The copper cylinder is fitted snugly into a stainless steel vacuum thermos, manufactured by Nissan. The system is heated by a thin Kapton-insulated thermafoil heater (Minco, Inc.), which is bonded to the exterior of the copper cylinder. Temperature feedback is supplied by a platinum RTD thermal ribbon (Minco, Inc.), also fixed to the cylinder. We have used either a proportional-integral controller (Wavelength Electronics RHM-4000) or a proportional-integral-derivative controller (Watlow 93 series) for temperature regulation. The system is shown in the accompanying block diagram (Fig. 1).

B. Flow and pressure regulation

In theory, the permeation rate of the source is independent of the flow conditions outside the permeation tube, provided there is a large concentration gradient across the permeation tube. However, because nitric acid (HNO_3) has a low vapor pressure and strong wall interactions, it is difficult
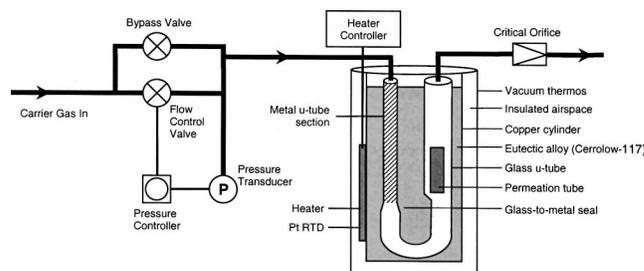

FIG. 1. Block diagram showing the permeation device. The eutectic alloy is contained in a copper cylinder, with a temperature sensor and heater attached to the exterior. The permeation tube is held in a glass *u*-tube inserted into the eutectic alloy. The temperature-controlled components are insulated by a vacuum thermos.

to handle quantitatively. Our laboratory tests have indicated that both constant pressure and constant carrier gas flow rate increase calibration source stability. For this reason, we have designed a flow system which controls pressure directly and volume flow rate indirectly. This is achieved by combining a pressure control loop and a glass critical orifice.

Dry nitrogen, supplied at 2000–4400 mb (1 mb=1 hPa), is used as the carrier gas. In the flight system, this carrier gas is provided by the boil-off of a liquid N_2 Dewar. Alternatively, the calibration system can be supplied with N_2 from a gas cylinder or Dewar in the lab. Flow and pressure are regulated by a control valve upstream of the permeation tube and a critical orifice downstream, as shown in Fig. 1. During normal powered operation, a capacitance manometer (MKS 750 series, range 4400 mb) senses the pressure downstream of the control and bypass valves. A proportional-integral controller (Wavelength Electronics RHM-4000) compares the measured pressure to a fixed set point and adjusts the control valve (MKS 148 series) accordingly to maintain the desired system pressure. A glass critical orifice, with a measured flow rate of 50 std cm^3 min^{-1} at 2000 mb absolute pressure, provides critical flow for external pressures up to ~1000 mb. When power is interrupted, the control valve closes, and a normally open TFE solenoid bypass valve (NResearch) allows carrier gas to flow through the system. The pressure in bypass mode is equal to the supply gas pressure. Although flow and pressure are not strictly controlled in bypass mode, the continued flow prevents the buildup of permeation gas in the glass *u*-tube and minimizes disturbance between the powered and unpowered states.

C. System requirements

The components and associated electronics shown in Fig. 1 fit easily into a portable $10 \times 18 \times 30$ cm^3 case, and into a smaller space when installed in the airborne chemical ionization mass spectrometer. The portable calibration system weighs only 2.9 kg. The calculated maximum current requirement is 1.0 A, but the system typically draws 0.2–0.3 A in practice.
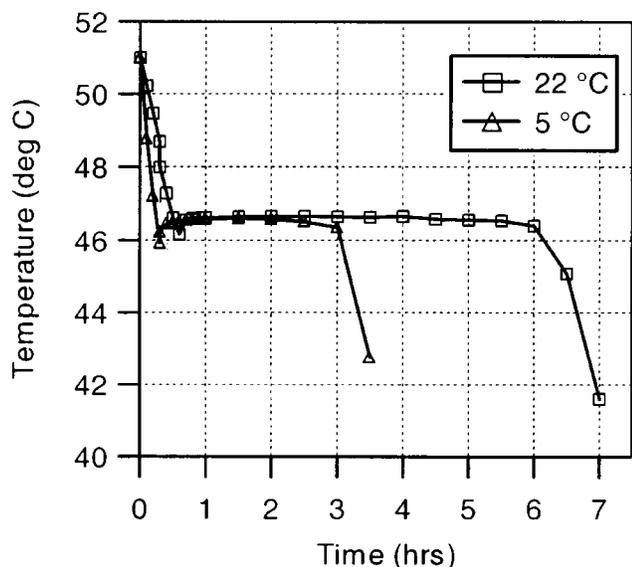
FIG. 2. Cooling of the eutectic alloy in the absence of external power. Two temperature profiles are shown, corresponding to external temperatures of 5 and 22 °C. At 22 °C, the phase change material maintains a temperature of 46.6±0.1 °C for over 5 h, after an initial undercooling to 46.2 °C.

III. PERFORMANCE

A. Temperature stability

The performance of the system was demonstrated by melting the eutectic alloy, inserting a platinum RTD directly into the alloy, and then monitoring temperature stability in the absence of power at two different ambient temperatures. These results are displayed in Fig. 2. When power is shut off at room temperature (22 °C), the system maintains a constant temperature of 46.6 °C for over 5 h. In a refrigerated container controlled to 5 °C, the system maintains a 46.6 °C temperature for more than 2 h. If necessary, additional insulation could be added around the thermos to reduce heat loss and increase this holding time. The observed difference from the reported Cerrolow-117 melting point of 47.2 °C is not critical in this application, since the phase change is stable and repeatable at 46.6 °C. During normal powered operation, the system is maintained at slightly above the eutectic melting point (i.e., 46.7 or 46.8 °C), and the temperature remains stable over many hours after the interruption of power. The largest temperature fluctuation results from a brief, initial undercooling. This undercooling lasts about 15 min at 22 °C, as the eutectic temperature drops to 46.2 °C before recovering to 46.6 °C. Undercooling is a fundamental property of eutectic bismuth alloys.[7] The undercooling implies an initial ΔT of 0.5–0.6 °C during solidification, resulting in at most a 5% decrease in permeation rate following the loss of power.

B. Permeation rate stability

The long-term stability of the system was monitored using ion chromatography (IC). Nitrate samples were collected by bubbling the HNO_3/N_2 gas mixture into water, immediately downstream of the critical orifice shown in Fig. 1. The HNO_3 gas mixture was collected by dissolution in prewashed volumetric vials containing approximately 10 mL of deionized water (Millipore Milli-Q system). Tests showed that
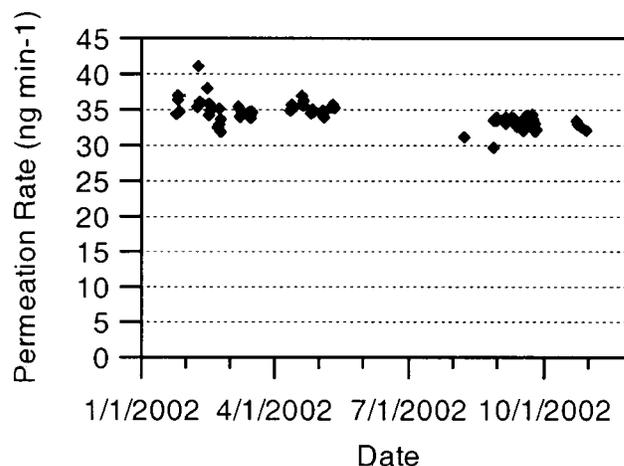

FIG. 3. Long-term stability of the permeation device over a 10 month period, as measured with ion chromatography. The average permeation rate is 34.2±1.6 ng min^{-1}.

this volume was adequate for complete collection of the nitrate. Sample collection times varied from 4.4 to 40 h, in order to keep the NO_3^- concentration well above the 5 μM detection limit of the IC. NO_3^- concentrations of these samples were measured using a DX 500 Dionex IC configured with an autosampler, gradient pump, anion self regenerating suppressor and KOH cartridge in an eluent generator, AS 11 IonPac column, and an ED40 electrochemical detector. Eluent (21 vol % of 5 mM NaOH solution) was run isocratically and concentrations were calibrated with NO_3^- standards made from KNO_3 salt. IC analyses were performed within 1 week of sample collection, although sample NO_3^- concentrations appeared to be stable over time. NO_3^- was the only negative ion detected in the samples. If other ions were present, they did not exceed the detection limit of the IC. The average permeation rate for each sample was calculated from the measured NO_3^- concentration, the sample volume, and the collection time.

Figure 3 shows the permeation rate measurements for one isotopically labeled $H^{14}N^{18}O_3$ tube over a 10 month period. The average permeation rate is 34.2 ng min^{-1} (222 ppbv in a 50 sccm flow of N_2) with a standard deviation of 1.6 ng min^{-1}. This error represents a combination of permeation rate drift and error in the sampling and analysis technique. Possible errors arise from uncertainty in the standard concentrations and the accuracy of water volume measurements. IC instrumental error is less than 1%, as estimated from repeated sample measurements.

C. Assessment

The temperature and permeation rate stability results show that this system is stable over time and during power interruptions of several hours. The initial undercooling of the eutectic alloy represents the main uncertainty in temperature regulation after power loss. The lightweight, compact design and temperature stability make this system ideal for field measurements.

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