PAMSGRAM

April 10, 1996

COMMENTS ON THE USE OF NAFION™ DRYERS IN PAMS

During a recent PAMS Measurements Work Group conference call, one of the topics discussed was a systematic way to monitor the performance of the water management system for PAMS autoGC systems. Specifically, the Nafion™ dryer that is a part of the widely used Perkin-Elmer autoGC was of interest. This dryer was originally tested by EPA in an autoGC system that was used to monitor the TO-14 set of toxic VOCs. The drying efficiency, sample integrity, and description of equipment were reported by Pleil, et al. (**JAPCA**, 1987) and the use of the dryer was recommended in the method TO-14 in the EPA ***Compendium of Methods for Toxic Compounds***. Subsequent use in EPA methods development programs has been successful for the TO-14 compounds. The application of the dryer was subsequently extended for use in detection of the PAMS target compounds. However, the lack of information about the transmission properties of the dryer for some of the PAMS compounds has resulted in concern about sample integrity and data quality. In particular, definitive information about α- and β- pinene and other unsaturated hydrocarbons has been missing. A protocol for checking the drying efficiency of the dryers has also been missing. These two issues are discussed as follows.

Basis for Drying Efficiency Protocol for Nafion™ Dryer

To determine the status of the drying efficiency for this dryer, the Methods Branch within the National Exposure Research Laboratory (NERL-ORD) proposes an in-line status monitor. The design objectives of this monitor along with the circuit diagram, a physical description of the unit, and the specifications of the integrated circuit humidity sensor chosen for the monitor are given in the attached draft description. As noted in the physical description, the humidity probe would be mounted in a "T" placed between the dryer and the preconcentration trap. A voltage readout indicates the level of humidity. To reduce cost, the system does not include a temperature measurement and does not give a relative humidity reading. The "RH" output is a voltage signal that would indicate acceptable performance for the dryer in a controlled environment typical of PAMS monitoring stations. This value will vary somewhat with temperature but this should not be a problematic issue.

The unit has been tested at various humidity levels with acceptable results. However, the unit sensor failed during the later stages of the testing and has been returned to the manufacturer for repair. Obviously, a period of testing for reliability during actual performance is necessary to recommend this unit for general use.

Alternatives: There are numerous commercial monitors that could be adapted for use as a status monitor for the dryer, including those that provide a true relative humidity reading. However, the probes for these units are too large to be installed in-line in current systems and are significantly more costly than the $500 estimated cost for the proposed unit.

If there is sufficient interest in this work, EPA will proceed in the testing of the unit on an autoGC system and fabricating copies for interested users in state agencies.

Removal/Transformation of Compounds on the PAMS List

The Nafion™ dryers are known to remove some oxygenated compounds and to cause rearrangement of monoterpenes as reported by Burns et al. (**J. Chromatography**, 1983). Other more recent information from Gong and Demerjian (**JA&WMA**, 1995) relates to the use of Nafion™ dryers on systems designed to monitor hydrocarbons in air. The problems reported when using the dryers at room temperature are minimum. However, using the dryer shortly after heating to remove residual water vapor, can significantly affect the sample integrity of C4-C6 alkenes (except cycloalkenes). C4 alkenes are reported to rearrange although the carbon count remains the same. The C5 compound isoprene is lost without reappearance of an equivalent amount of carbon. In the case of C6 alkenes, new unknown peaks emerged in the neighborhood of the original peaks. These effects are reversed if, after heating, the dryer is purged with clean N2 at a flow rate of 50 cc/min for 3 hrs. Fortunately, the Nafion™ dryer is not heated in typical PAMS installations.

Other experimental information (W.A. Lonneman, Proceedings of the **1994 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants**) shows that only four of the PAMS compounds are significantly affected by a Nafion™ dryer. Both α and β-pinene are completely removed (and/or converted) by a Nafion™ dryer operated at room temperature. 2-methyl-1-pentene and styrene concentrations are reduced significantly although the appearance of additional compounds may account for some of the carbon. In real-world mixtures, polar VOCs showing tailing peaks on the GC trace are reduced or eliminated; the analysis of one sample showed that MTBE was completely removed by the Nafion™ dryer.

The above results and other less documented laboratory experiments support the view that a PAMS protocol for using the dryers should be observed. The dryers may vary from batch to batch and could experience a change in transmission properties with aging. Clearly, heating of the dryer in the PAMS applications should be avoided. The dryer should be tested initially and at periodic intervals (weekly) for transmission of the target compounds using realistic test samples, i.e. humidified air samples containing PAMS target compounds at concentrations expected in the air. To do this, each station would need a reference gas cylinder of the PAMS target compounds on hand along with some type of dilution system (assuming the reference gas cylinder concentration must be diluted into the typical ambient concentration range) including a way to humidify the test gas stream.

Sensor Description

A design for a humidity sensor has been developed by the Mantech Environmental Technology Inc. (METI) support contractor for the Methods Branch, AMRD, NERL and is outlined on the attached pages. It is based on the integrated circuit humidity sensor Model IH-3605 manufactured by HYCAL of El Monte, California.

Comments

Comments on this paper should be directed to:

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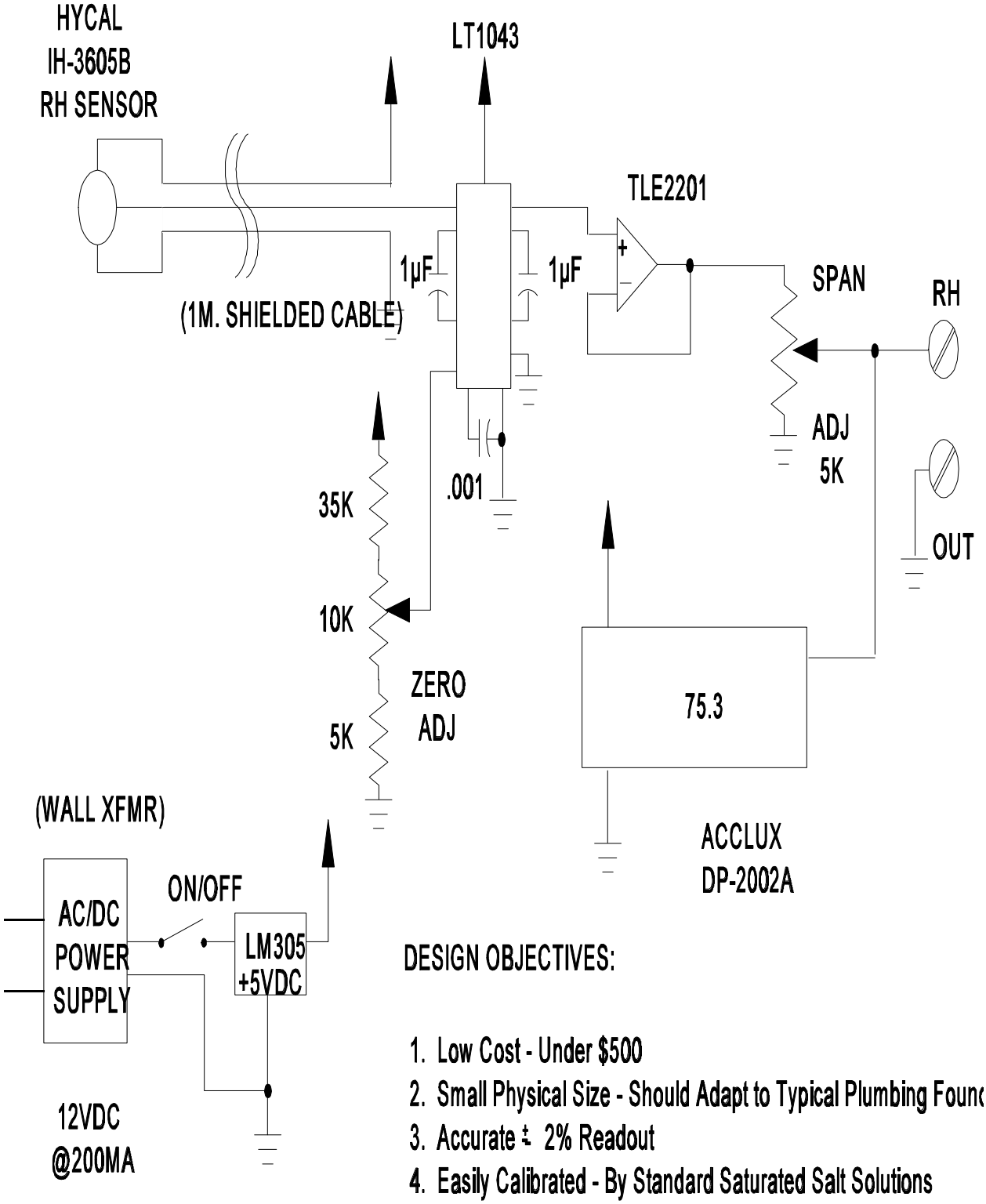
CIRCUIT DIAGRAM



DESIGN OBJECTIVES:

1. Low Cost - Under $500
2. Small Physical Size - Should Adapt to Typical Plumbing Fount
3. Accurate ± 2% Readout
4. Easily Calibrated - By Standard Saturated Salt Solutions
5. Low Maintenance - Probe Replaceable

PHYSICAL DESCRIPTION