Technical Papers of ISA

ISA–The Instrumentation, Systems, and Automation Society

Proceedings of the 46th Annual ISA Analysis Division Symposium

Volume 34

Presented at:
The Radisson Hotel & Conference Center
Houston, Texas, USA
22-26 April 2001

ISA Volume 410

Sponsored by ISA and
ISA ANALYSIS DIVISION

VOLATILE ORGANIC COMPOUND (VOC) ANALYZER FOR COOLING TOWER WATER

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KEYWORDS

VOC, Cooling Tower, Heat Exchanger Leaks, Fugitive Emissions, Waste Water

ABSTRACT

This is an in plant case study of a Model 204 volatile organic compound (VOC) in water analyzer. The system uses membrane sample transfer to separate VOC from cooling tower water. The water flows past one side of a membrane. The VOC permeates through the membrane into a clean dry carrier gas flowing past the other side of the membrane (1). This clean sample is ideal for readout using a solid state sensor, gas chromatograph, mass spectrometer, infra red or other readout. In plant on line chart recordings are shown that illustrate development of heat exchanger leaks and the response time to correct leaks at the one part per billion by weight (ppbw) level in an ethylene plant.

INTRODUCTION

Continuous on line analysis measures VOC in cooling tower water, wastewater or steam. Weld ruptures or corrosion leaks in heat exchangers can result in massive quantities of VOC being dissolved in cooling tower water. Better than 99 % of VOC in cooling tower water is striped out in the cooling tower. Continuous on line monitoring can pay for itself in savings of lost product and labor. An average refinery of 330,00 barrels per day, without VOC monitoring, was found to leak 1,600 pounds per day (lb/day) about 700 ppbw. With monitoring and control, leaks are to be limited to 84 ppb or less for all VOC's (2). Obviously equipment corrosion or rupture could result in leaks totaling many thousands of lbs/day of VOC vapor from a cooling tower which will be invisible in the air above the tower.

SYSTEM DESCRIPTION

This study describes equipment installed in an air-conditioned instrument enclosure. This allows one ppbw measurement. A sample preparation system was selected to prevent contamination of the analyzer system, see Figure 1. The sample passes by one side of a permeable membrane. VOCs dissolve in the membrane then permeate through into a clean dry carrier gas flowing past the other side of the membrane. To avoid deterioration of grab samples, used in laboratory analysis, the system includes an automatic permeation tube calibration system to validate analyzer response (3) (4). Incorporation of a microinjection calibrator, for verification, was used for additional proof of dependable measurements near one ppbw. Local digital readout, as well as a 4-20 ma signal for control room monitoring, were incorporated. The complete system is fully automatic with validation, alarm and monitoring by only the control room operator. Redundant readout solid-state sensor and GC was used. This gives a total VOC as benzene by sensor and benzene only readout by GC. This helps to identify the leaking heat exchanger.

VALIDATION OF DATA

The analyzer system, pre-fabricated and calibrated for drop in place installation, was delivered to an ethylene plant in Corpus Christy Texas in March of 1997. Both the solid state sensor readout and the GC readout were operational when power was applied. On March 10, 1997 a test of the two calibration systems, built into the analyzer system, were activated. See Figure 2. The sold state sensor and the GC readout had been factory calibrated using a sample prepared by mixing pure benzene in distilled water as reference sample. The chart recording of the base line is within one ppbw. The permeation tube furnished as a 20 ppbw reference read within one ppbw and the microinjection validation sample set for 10 ppbw responded within 2 ppbw. The design was to control benzene level not to exceed 5 ppbw, the allowable benzene limit.(5)

ON LINE DATA

Figure 3 illustrates a three-day on line measurement of benzene level in cooling tower water as it enters the cooling tower. The GC readout is specific for benzene VOC only. The solid state tin oxide sensor, which was also installed, responds to all VOC's. The recording is of benzene concentration only by GC. Background noise is seen to be approximately ± 1/2 ppbw.

A chart recording of process water benzene concentration, during a three-day period, is shown in Figure 3. After twelve hours running time a leak began to develop in a heat exchanger. At a level of 2 ppbw corrective action had been taken and benzene concentration began to decrease. As is apparent from the recording less than 30 minutes elapsed from the time the leak was detected and the maintenance action was completed. Within one and one half-hours all benzene had been stripped by the cooling tower from the cooling tower water. The steady state size of this leak cannot be determined from the record.

A second leak, probably in another heat exchanger was found about 19 hours later. This leak was developing more slowly. Corrective action was again taken at the one ppbw level with recovery to the baseline in about the same length of time. As shown by the subsequent lowering of the base line, this heat exchanger apparently had a one half ppbw long term leak that was also eliminated.

CONCLUSION

This analyzer system proved to more than meet the design requirements, which was to control benzene in cooling tower water at the five ppbw level. Validation of data was accomplished by incorporation of two calibration methods, both automatic or manually activated. The built in permeation tube calibrator was supported by an innovative microinjection system which generated ppbw sample standard by direct injection of benzene into a flowing clean water steam. A solid state readout provided a measure of total VOC as benzene and a gas chromatograph measured benzene directly. Four years of continuous on line operation in an operating ethylene plant is proof that it is practical to measure VOC in cooling tower water or waste water treatment systems at low ppbw levels.

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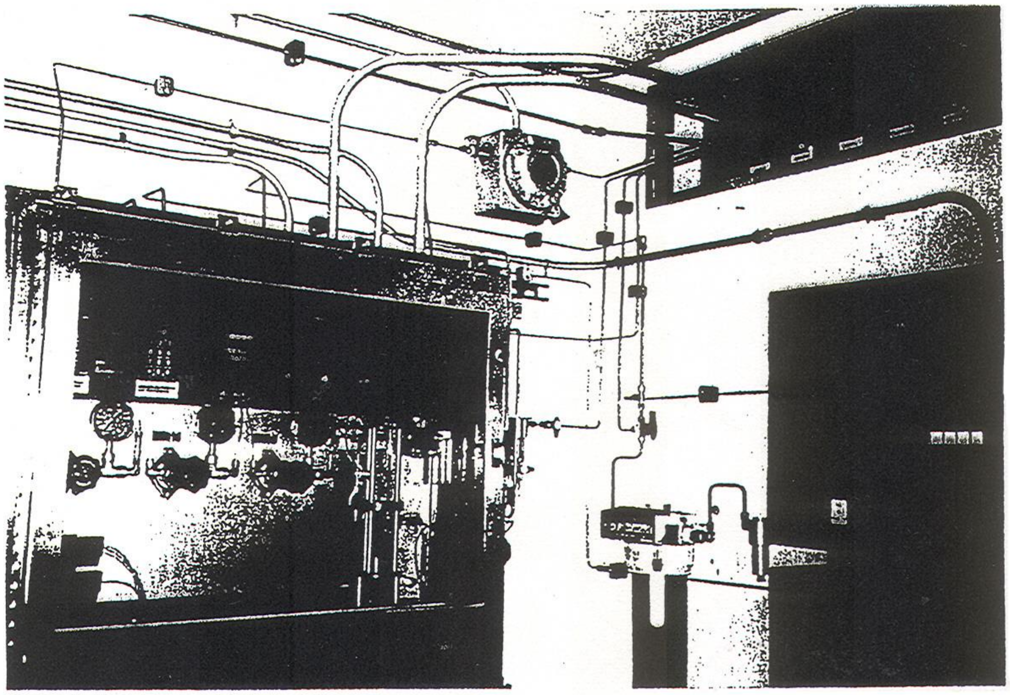
5. `Texas Natural Resources Conservation Commission (TNRCC) determined that this installation conforms to "Best Available Control Technology (BACT).



MEMBRANE SAMPLE TRANSFER SENSOR AND TWO CALIBRATORS

GAS CHROMATOGRAPH USING MEMBRANE SAMPLE

Fig. 1 COMPLETE ANALYSIS SYSTEM

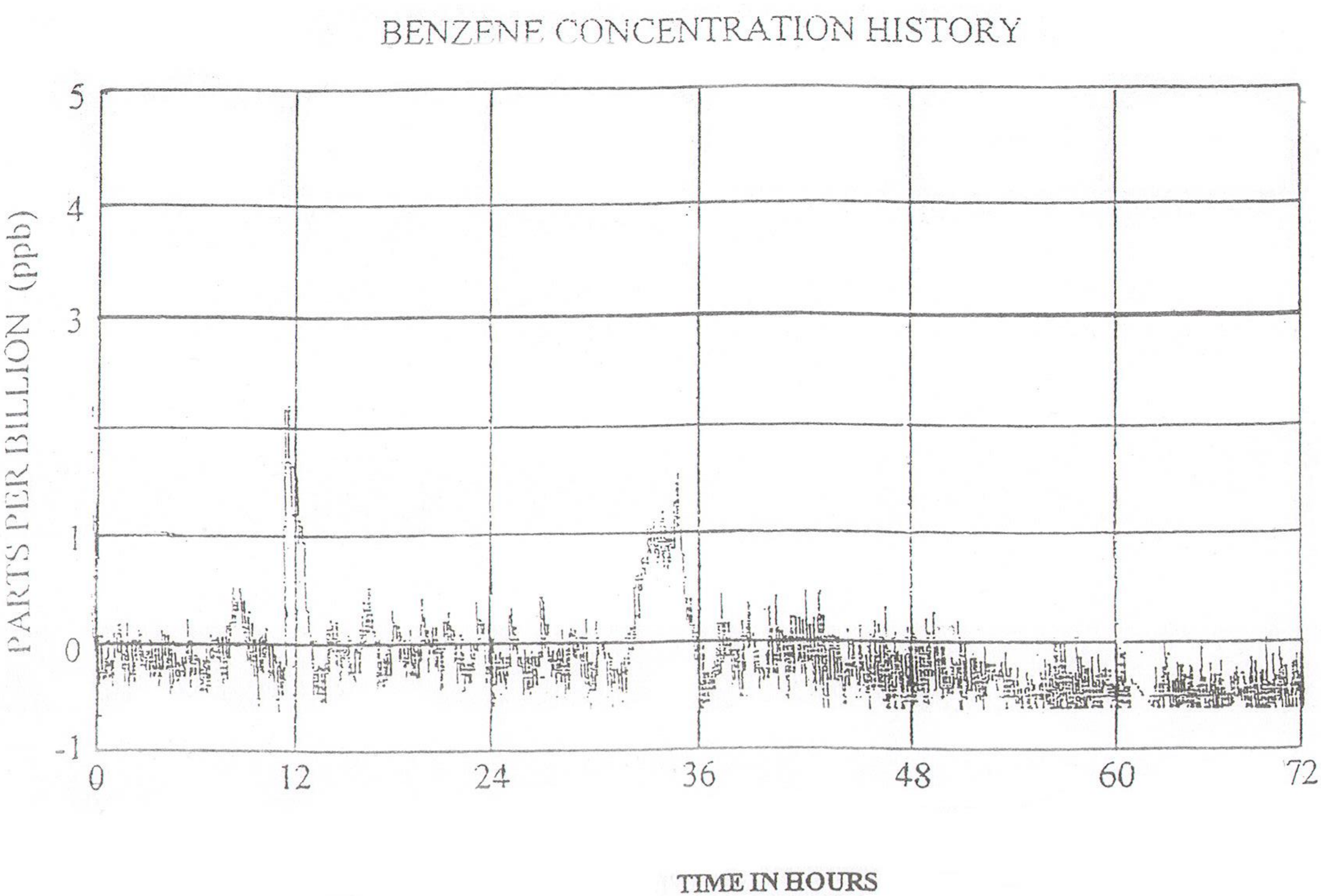


Fig 3. ETHYLENE PLANT COOLING TOWER WATER

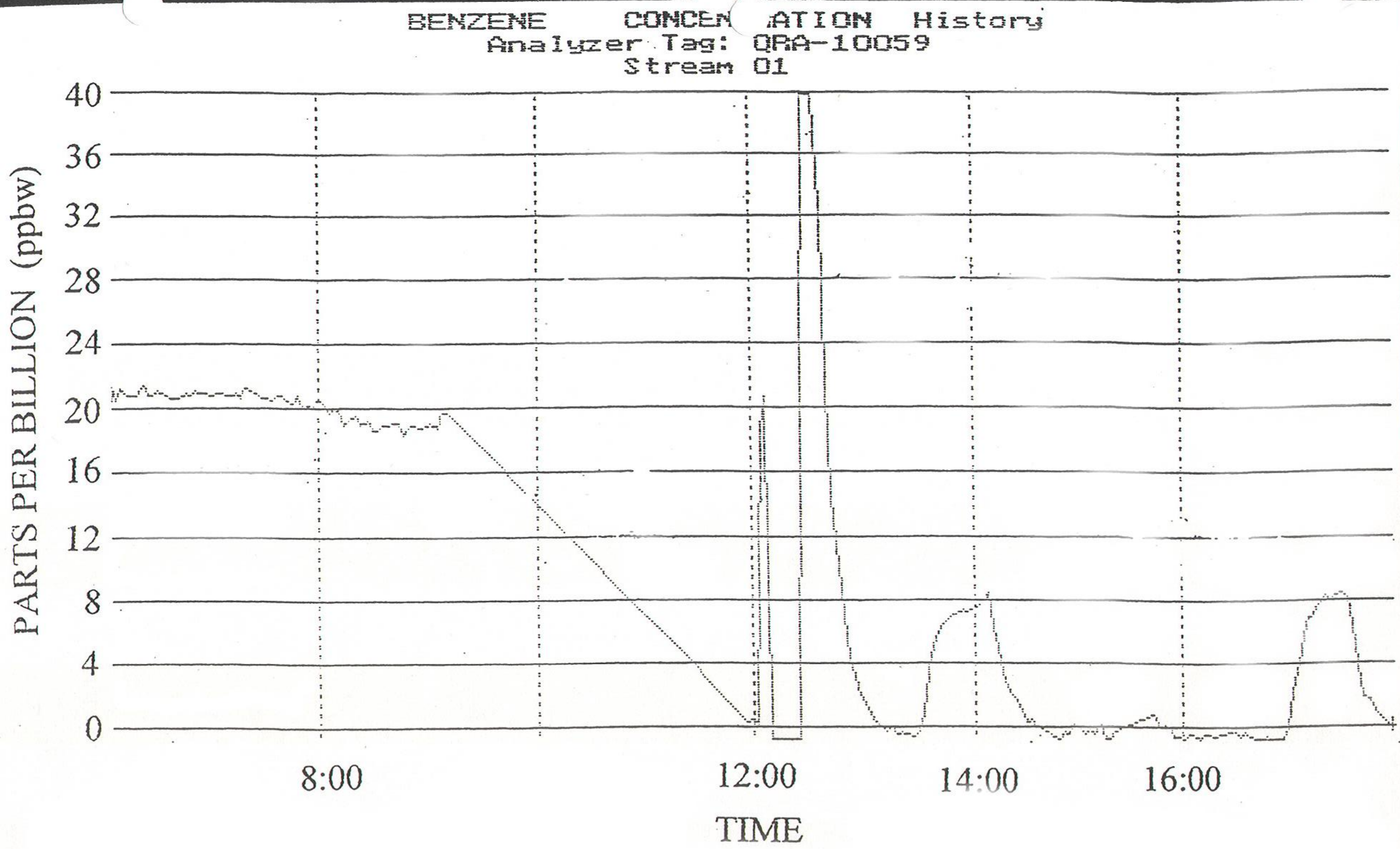
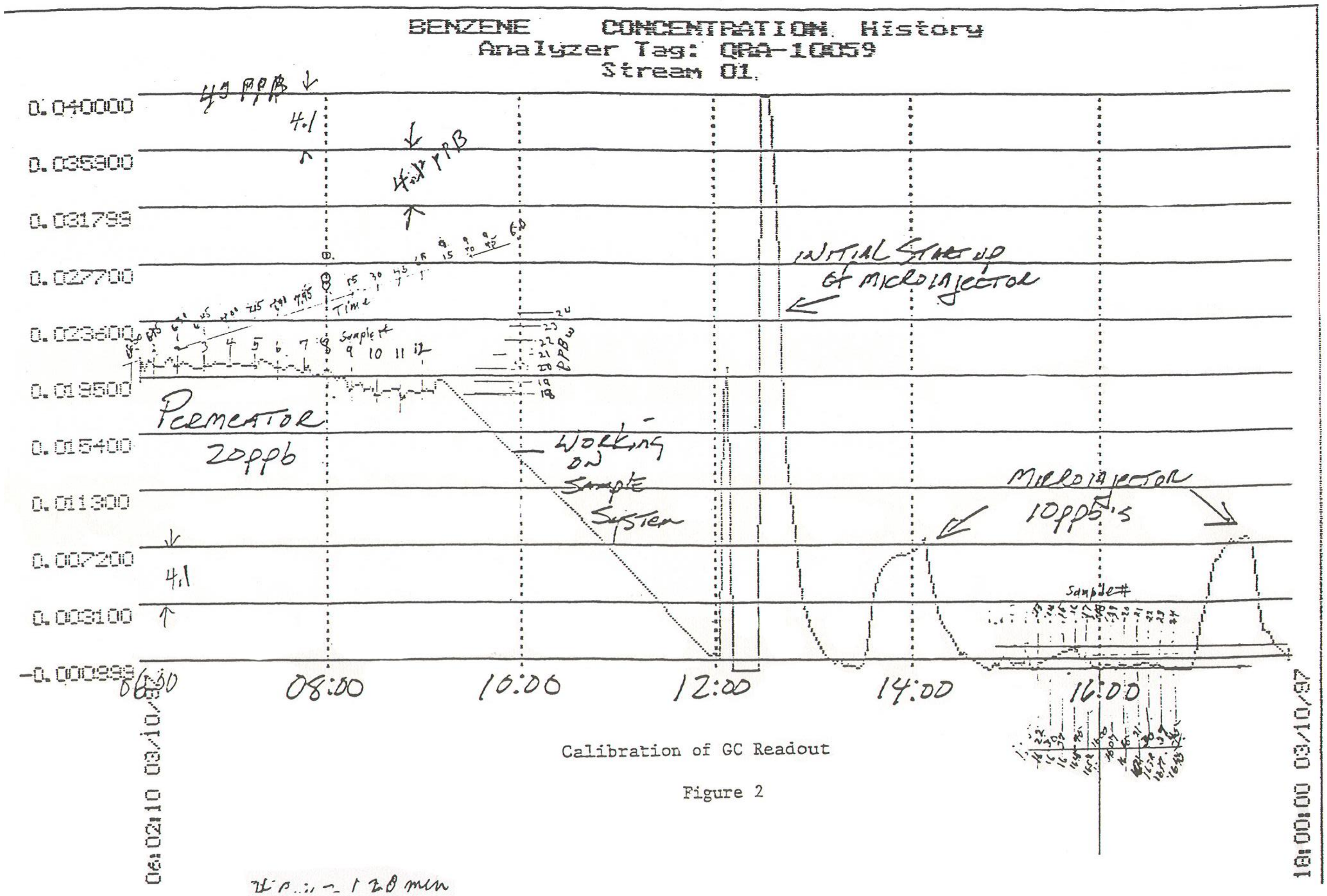


Fig. 2 **ANALYZER VALIDATION BY PERMEATION TUBE AND BY MICRO INJECTION OF BENZENE**



Calibration of GC Readout

Figure 2