Using the OI pH*Detect* to Automate pH Determination After Running VOC's by P&T GCMS

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1. Introduction

Commercial laboratories are required to verify that samples were preserved properly prior to analysis of laboratory samples. An exception is Volatile Organic Compound (VOC) analysis where to avoid loss of VOCs pH must be determined after the test is completed. This pH check requires opening each sample vial, immersing a pH strip or paper, and estimating the pH. This extra step is time consuming and a burden to the laboratory. The OI Analytical (OI) pH*Detect* automates pH determination by adding a pH probe between the purge vessel and waste collection. This poster presents time saving and analysis results of our evaluation of the pH*Detect.*

2. Experimental

Operating Principles of the pH*Detect*

As the water sample drains from the OI Purge and Trap sparge vessel, it is collected in a glass reservoir (Figure 1) on the pHDetect module where a glass pH electrode takes a pH reading. The pH reading is logged with a date and time stamp (Figure 2) in the auto-sampler data base that is easily linked to the instrument run-log (Figure 3) correlating each vial to its corresponding sample number or identification. This creates a permanent record of pH measurement eliminating transcription errors and inaccuracy associated with pH paper measurement.

Calibration of the pH electrode is fully automated and performed at user programmable intervals using two buffers intended to most closely match the expected pH of the samples. All calibrations are logged with a date and time stamp.

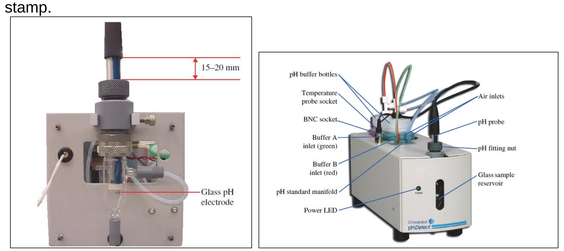

Figure 1 Close-up of the pH*Detect* electrode module alongside a picture of the entire module

Date/Time of Entry	User ID	Log Entry Details
4/1/2019 12:48:40PM	OIC4660	vial pos 1, pH = 5.7, last cal 04/01/2019 (pos-> position)
4/1/2019 1:11:22PM	OIC4660	vial pos 2, pH = 6.0, last cal 04/01/2019 (pos-> position)
4/1/2019 1:33:35PM	OIC4660	vial pos 3, pH = 6.4, last cal 04/01/2019 (pos-> position)
4/1/2019 1:55:09PM	OIC4660	vial pos 4, pH = 7.3, last cal 04/01/2019 (pos-> position)
4/1/2019 2:18:25PM	OIC4660	vial pos 5, pH = 7.0, last cal 04/01/2019 (pos-> position)
4/1/2019 2:41:03PM	OIC4660	vial pos 6, pH = 7.5, last cal 04/01/2019 (pos-> position)
4/1/2019 3:03:43PM	OIC4660	vial pos 7, pH = 8.2, last cal 04/01/2019 (pos-> position)
4/1/2019 3:26:23PM	OIC4660	vial pos 8, pH = 8.3, last cal 04/01/2019 (pos-> position)
4/1/2019 3:48:32PM	OIC4660	vial pos 9, pH = 7.6, last cal 04/01/2019 (pos-> position)
4/1/2019 4:11:07PM	OIC4660	vial pos 10, pH = 7.3, last cal 04/01/2019 (pos-> position)
4/1/2019 4:33:45PM	OIC4660	vial pos 11, pH = 7.1, last cal 04/01/2019 (pos-> position)
4/1/2019 4:56:46PM	OIC4660	vial pos 12, pH = 6.9, last cal 04/01/2019 (pos-> position)

Figure 2 Data output of the pHDetect showing date, time, vial position, and pH

11	7	0401vn011.d	1.	-MRLCHK_0.50ppb thm std	ull032619; vis011419	1 Apr 2019 11:47
12	8	0401vn012.d	1.	-MBLK_LRB	vis011419	1 Apr 2019 12:09
13	1	0401vn013.d	1.	201903280705	@thm524; vis011419	1 Apr 2019 12:43
14	2	0401vn014.d	1.	201903280706	@thm524; vis011419	1 Apr 2019 13:06
15	3	0401vn015.d	1.	201903290453	@thm524; vis011419	1 Apr 2019 13:28
16	4	0401vn016.d	1.	201903280018	@thm524; vis011419	1 Apr 2019 13:51
17	5	0401vn017.d	1.	201903290560	@thm524; vis011419	1 Apr 2019 14:13
18	6	0401vn018.d	1.	201903290454	@thm524; vis011419	1 Apr 2019 14:36
19	7	0401vn019.d	1.	201903290455	@thm524; vis011419	1 Apr 2019 14:58
20	8	0401vn020.d	1.	201903290456	@thm524; vis011419	1 Apr 2019 15:21

Figure 3 Instrument run log with vial numbers circled corresponding to Figure 2

Using pH paper is an inexpensive and relatively accurate way of estimating the pH of an aqueous liquid. To prepare pH paper, a strip of filter paper is soaked with different pH indicators, or a mixture of indicators (universal indicator), and allowed to dry. Touching solution to the paper or dipping the paper in solution causes the color of the indicator on the paper to change according to the pH. The color and relative intensity of the color is compared to a chart from which pH is estimated. Using only one indicator per paper enables a better estimate of a narrow pH range.

pH strips are more rugged than pH paper and consist of one or more (usually up to four) small squares or rectangles of pH paper attached to one end that is dipped into the sample. Each square is impregnated with a different pH indicator resulting in different colors and intensity in relation to the pH. The color and intensity of each square is compared to a chart from which pH is estimated. The different indicators/colors of each square provide users with greater confidence in their estimation of the pH.

Measuring pH with pH paper and strips are screening methods that are only capable of indicating pH. In addition, they are very subjective and can suffer lot-to-lot, within lot variability, and as shown in Figure 4 often do not produce equivalent results. Data in Figure 4 were collected by different analysts on different days on different samples as received at the laboratory. Narrow range pH strips, believed to be more accurate, were used.

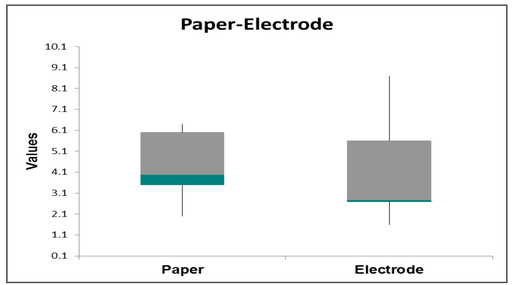

Figure 4 Equivalency Box Plot showing non equivalent results of pH samples measured using pH strips and compared to the Electrode Method.

In this study, the pHDetect is approached as a screening method to obtain results as good as, or better than possible using paper and eliminating the need of analysts to open each vial, immerse a pH strip, read and record the result. Thus, even though the pHDetect is capable of routine auto-calibration, batch-to-batch calibration should not be necessary. Even so, in our experiments and cost evaluation, we calibrated at the beginning of each analysis of two batches.

The auto-sampler was loaded with vials containing thiosulfate preserved trihalomethane samples. This preservative only removes residual chlorine so the expected pH is that of finished drinking water, or 6.5 to 8.5. Next, these samples were followed by HCL preserved samples with an expected pH of less than 2. These were immediately followed by samples with ascorbic acid only, to simulate samples where the HCL was inadvertently not added.

3. Results and Discussion

The pH detect was able to adequately indicate the drop in pH of neutral samples to samples containing HCL at pH < 2. (Figure 5) In addition, simulated samples containing only ascorbic acid and no HCL were readily recognizable. The first ascorbic acid only sample read pH 2.7 followed by its duplicate at pH 3.3 indicating there may be some carryover, however, these two readings are well within the expected accuracy of narrow range pH paper or strips (Figure 4).

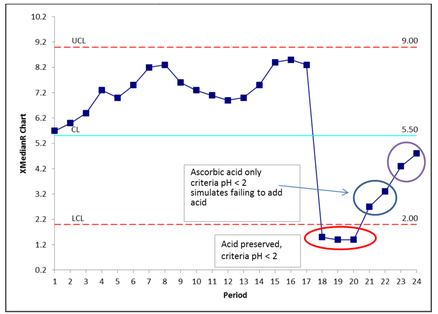

Figure 5 Equivalency Box Plot showing non equivalent results of pH samples measured using pH strips and compared to the Electrode Method.

3. Conclusion

Installing an OI pHDetect after an OI Purge and Trap makes it possible to verify the preservation of samples being run for volatile organics. Measurements are as accurate as by pH paper or strips and eliminate the labor required to remove and open each vial, immerse a strip, wait for color to form, estimate the pH and record the result. In addition, unlike manually recording pH, there is an unalterable data trail with results permanently recorded with date and time by vial number in the OI Purge and Trap software.