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A Method for the Determination of Strong-Acid Vapors in the PPM Range

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ABSTRACT

A nondiscriminating method for the quantitative detection of strong-acid vapors has been developed. The colors produced by passing known volumes of suspect air through disks of filter paper impregnated with an acid-sensitive reagent are compared with the colors on a calibrated reference chart. Reproducible sampling and analysis are accomplished in less than one minute with one to five strokes (100-500 cc) of a bellows-type hand pump. The range of the method as presently calibrated is 0.2 to 40.0 ppm by volume as monobasic gas.

PROBLEM STATUS

This is a final report on this phase of the problem; work in other areas is continuing.

AUTHORIZATION

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A METHOD FOR THE DETERMINATION OF STRONG-ACID VAPORS IN THE PPM RANGE

INTRODUCTION

A recent project concerned with gas absorbents required frequent analysis of the feed stream for acid-gas contaminant in the parts-per-million range. The wet chemical analytical technique used, while accurate, was laborious and time-consuming. A semi-quantitative procedure utilizing pH test paper strips was developed, empirically calibrated, and successfully applied to the problem. This technique has been modified and improved by the substitution of acid indicator impregnated filter paper for nonporous pH-paper strips. This change permits sampling of known volumes of suspect air, thus quantifying the results and making the technique applicable to nearly all sampling conditions.

An additional modification was the development of a comparative color chart for concentration evaluation. The pH test strips used for screening tests have accompanying color charts, calibrated in pH units, based on the appearance of the test strips following immersion in aqueous solutions. While similar, the colors produced on these strips by "dry" exposure to strong acid vapors in air are sufficiently different in hue and variety to warrant the use of a different chart. The development and calibration of such a chart was an important part of this problem.

Sensitivity screening tests utilized seven commercially available pH test paper strips: wide-range (2-10 pH) Alkacid*, narrow-range (0-3 pH) Alkacid, wide-range (1-11 pH) Hydrion*, narrow-range (0-1.5 pH) Hydrion, narrow-range (1-2.5 pH) Hydrion, narrow-range (3-5.5 pH) Hydrion, and Vivid (0.0-9.0 pH) Hydrion. Under the test conditions, only the two wide-range papers, the 1-2.5 pH narrow-range Hydrion paper, and the 0-9 pH Vivid Hydrion paper were acid-gas sensitive, with the 1-2.5 pH range paper being superior to all. This report will deal with the further development of this latter paper as a quantitative detector for strong-acid gases in air.

SAMPLING PHILOSOPHY AND TECHNIQUE

In order to relate exact acid-gas concentrations to the color changes produced on the test paper strips previously used empirically, a means of controlling and measuring the volume of contaminated air contacting the indicator was required. The most obvious method for accomplishing this was to pass a measured volume through a porous paper disk impregnated with the acid-indicating chemical.

Laboratory application of aqueous meta-cresol purple solutions to various grades of filter paper confirmed the feasibility of the sampling technique, but nonuniformity between prepared batches of paper gave poor reproducibility in the data. It was learned from the Hydrion manufacturer† that 20 × 20 inch sheets of filter paper, uniformly impregnated with the indicator used on their 1-2.5 pH paper strips, were stock items with the company. Sample sheets were obtained for testing.

*Registered trademark.

†Micro Essential Laboratory, Brooklyn, N. Y.

The success of this method also depends upon a sample being presented uniformly to a constant area of paper in a relatively short time interval — long sampling time integrates fluctuating concentrations and allows interface reactions to affect the test adversely. For these reasons, a pumped sampling technique was selected. A hand-operated 100-cc-per-stroke, bellows-type suction pump* was selected for reasons of operational simplicity and versatility.

Initial testing was with 1-inch circles punched from the test paper sheets and supported in an open-face aerosol filter holder adapted with tubulation for insertion in the inlet of the pump. This early work, while proving the feasibility of the method, indicated that increased sensitivity and reproducibility would result from the use of a smaller reactive area. Subsequent work and final calibration were performed using 7/16-inch circles. The exposed, or effective, area of these disks has a diameter of 5/16 inch.

SENSITIVITY TESTS

For ease of production and control, HCl was selected as the test gas. The main stream of air was passed at 4 liters/min through a humidity-control vessel and into small chamber, where it was mixed with an appropriately metered side-stream of air containing HCl. This mixture, monitored periodically by wet chemical titration, was passed into a 20-liter equilibration and sampling chamber. The atmosphere in the latter chamber was agitated by a paddle-fan and vented in such a manner that HCl concentration changes equilibrated within 20-30 minutes.

The HCl in the side air stream was obtained by passing a metered flow of line air through a sparger tube immersed in diluted aqueous HCl solution (2 parts acid to 1 part water). Air flow was monitored on a low-range rotameter but was measured with a soap-bubble flowmeter.

HCl concentrations in the sampling chamber were measured by a gas-liquid titration technique. A known volume of 0.001 N NaOH solution containing brom-cresol green indicator was exposed to a metered flow of the contaminated air stream for a length of time necessary to effect the end-point change. Appropriate calculations then gave the HCl concentration in ppm by volume. (The dilute solutions used for this titration technique require carefully adjusted and matched end points. While the nominal color change for brom-cresol green is blue to yellow, best results were obtained in this study by working to and from an intermediate blue-green color.)

Screening and familiarization tests using the 1-inch disks established that detectable color changes were produced by 100-cc (one-stroke) samples of air containing over 1 ppm HCl vapor. This quantity could be sampled in approximately 4 seconds, the paper's porosity being rate controlling. The colors produced were concentration related, and, by appropriate sampling, could be matched reasonably well against the color chart furnished with the test paper. These colors range in four steps from yellow-orange in the original paper to cerise, which indicates an aqueous pH of 1.0 on the chart.

The data leading to a feasibility decision are presented in Table 1. It is evident from these data that this technique has good sensitivity and is not markedly affected by moderate changes in temperature and humidity. Very low humidities, unlikely to be encountered in most applications, apparently lower the sensitivity somewhat, particularly upon extended sampling time at low acid concentrations. This effect may be related to a faster color fade rate in dry air, which will be discussed later.

*Draegerwerk, Lubeck, Germany. Available from Scott Aviation Corp., Lancaster, N. Y.

Table 1
Feasibility Tests

Run No.	Temp. (°C)	R.H. (%)	HCl Conc. (ppm-Vol.)	Pump Strokes*			
				Orange (2.5)	Red-Orange (2.0)	Orange-Red (1.5)	Cerise (1.0)
1	25	26	0.7	2	5	30	60
2	25	70	1.3	1	4	20	40
3	25	5	1.7	1	4	40	100
4	25	70	2.5	1	2	8	16
5	25	40	2.5	1	2	8	16
6	56	10	2.5	1	2	9	16
7	26	55	3.0	-	1	8	15
8	25	40	7.0	-	1	3	6
9	24	5	7.5	-	1	3	7
10	25	45	11.	-	1	2	4
11	25	80	11.	-	1	2	4
12	25	5	14.	-	1	2	5
13	25	45	18.	-	-	1	3
14	25	45	18.	-	-	1	3
15	26	10	20.	-	-	1	3
16	25	40	22.	-	-	1	3
17	50	10	25.	-	-	1	2
18	25	45	30.	-	-	1	2
19	25	45	36	-	-	1	2
20	25	80	45	-	-	-	1
21†	25	5	14	-	100cc	200cc	400cc
22‡	25	5	14	-	-	1 min.	-
23‡	25	40	7	-	1 min.	-	-

*Number of 100-cc strokes to produce indicated colors on aqueous pH chart furnished with Hydrion paper strips. Numbers in parentheses refer to aqueous pH on this chart.

†Continuously pumped and metered sample.

‡Paper disks held (dormant exposure) in sample chamber.

Run 21 demonstrates that continuous pumping, as opposed to the sequential hand-pump operation, has a small effect on the calibration, probably because the pumping rate was 800 cc/min, whereas the rate with the hand pump was about 1500 cc/min. This difference would allow the exposure-time effect shown by runs 22 and 23 to influence the color development.

APPARATUS AND CALIBRATION

These preliminary runs made obvious the need for a more varied color comparison chart. The color responses were such that small acid concentration changes gave reproducible tints that were intermediate between the four color tabs provided on the aqueous pH chart. It was also apparent that significantly greater sensitivity to low concentrations would result from the use of smaller disks, thus increasing the exposure per unit area of paper.

Disk holders for 7/16 to 1/2 inch circles were constructed to the dimensions shown in Fig. 1. In this configuration, the disks are self-supporting and no backup screen is

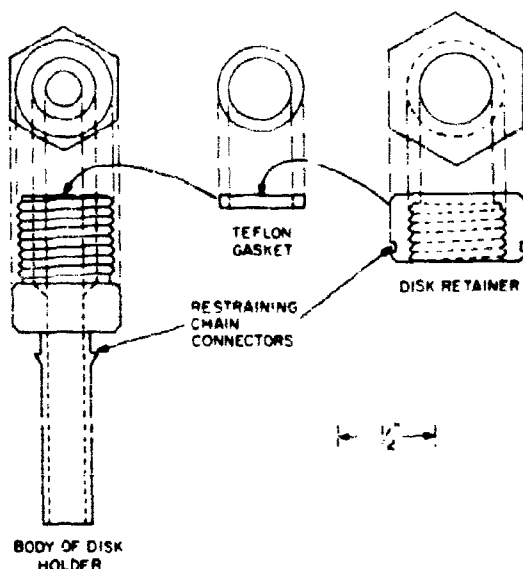


Fig. 1 - Filter disk holder details

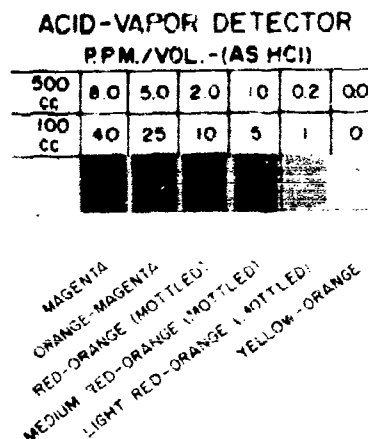


Fig. 2 - Concentration vs. color chart

required. The disks are easily loaded and the Teflon seal prevents bypass leakage. The 1/4-inch tubulation is adaptable to direct insertion in most hand pumps or to rubber tubing connection for remote sampling.

Using the smaller paper disks, a series of runs were made in which the colors developed by 100-cc samples at selected HCl concentrations were matched against selected colors on a multi-color printing chart.* These colors were then matched in paint and reproduced on appropriately calibrated cards by the Graphic Arts Branch of the Technical Information Division at NRL. The resulting cards were sealed in plastic for protection and ease of handling (Fig. 2). The complete analysis unit is shown in Fig. 3.

INTERFERENCES - CHEMICAL AND MECHANICAL

The test paper is unaffected by "normal" air, by test "garbage" air containing 1% CO₂, 37 ppm H₂, 75 ppm CO, and 130 ppm Freon-12, and by up to 100% CO₂. It is also unresponsive to vapors of weak acids such as acetic acid. High concentrations of basic gases such as ammonia and monoethanolamine produce a purplish-gray color which fades quickly back to the original color. Strong acid gases, such as HNO₃ and H₂SO₄, are indistinguishable from HCl. (Present calibration is based on ppm by volume as monobasic vapor. In the event that the acid species is dibasic, the ppm equivalent would be half of the apparent value.)

Although not truly an interference, the limited stability of the colors developed by this test procedure bears discussion at this point. Under all conditions tested, the colors fade rather rapidly - eventually returning to near the original shade of the unexposed paper. Fading, to some extent, appears to be a function of the concentration, low readings fading the fastest. This is probably an artifact resulting from the fact that small changes at higher concentrations produce less contrast, and consequently, less apparent fading. Because of the above, the comparison of the exposed color disk with the color chart should be made as soon as possible, preferably within 1 minute of the time of exposure.

*Marans 4-COLOR PROCESS OFFSET PRINTING CHART.

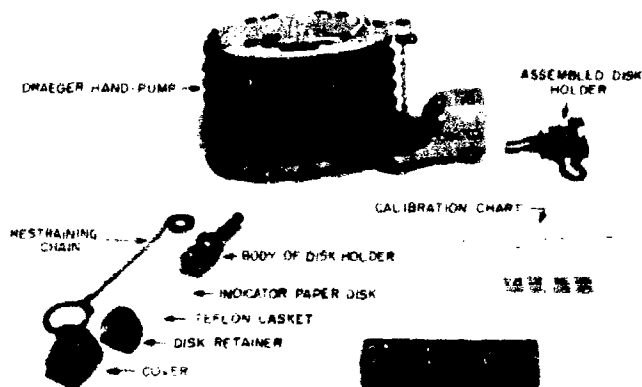


Fig. 3 - Complete analysis unit

Prolonged sampling, such as might be done for concentrations below 1 ppm, will include a "fade-rate" factor which could obscure very low contamination levels. Sampling under such conditions should be at as high a rate as possible (1-5 liters/min), so as to obtain a readable color contrast in a minimum time. (It should be pointed out that a 1-liter sample at 0.1 ppm HCl should give the same color as a 0.1 liter sample at 1 ppm HCl, etc.)

The humidity of the sampled air affects the calibration to a small degree and the fade-rate to a somewhat greater degree. Table 1 shows that all runs made at low humidity required somewhat larger samples to obtain the color development exhibited under wetter conditions. This was particularly evident in the 1-2 ppm range. The fade-rate of these "dry" disks was also appreciably faster than the "wet" ones. Since it is unlikely that actual testing will be done under such dry conditions as were these tests, this effect can be ignored. In any event, the 100 cc samples gave reasonable agreement regardless of the humidity conditions.

PRECAUTIONS IN STORAGE AND SAMPLING

The acid-sensitive indicator used in the paper disks will respond to very low concentrations of acid under conditions of long-time continuous exposure. Controlled storage tests revealed that acceptable container materials were very limited in number; metal, glass, rigid plastics, and foil-lined paper were nonreactive, while paper and all flexible plastics tested caused serious reddening of test disks after exposure times of from 1 to 10 days. Similarly, exposure to alkaline conditions or to excessive moisture, such as moist fingers, destroys the usefulness of the disks. Storage of a limited number of disks in each of several metal or plastic vials, and handling with metal tweezers, is recommended.

As demonstrated by runs 22 and 23 in Table 1, the test paper will respond to open exposure in a contaminated atmosphere. For this reason, the test disks must be stored in a sealed container in an uncontaminated area. The disk holder and pump should be loaded in a clean atmosphere and the open end of the holder covered until just prior to drawing the sample, after which the covering should be replaced while the disk is again taken to a clean atmosphere for color comparison. (A detachable cover, similar to a camera lens cap (Fig. 3), is recommended for this purpose.)

The above precautions are not as stringent if sampling is from a duct or otherwise confined stream or body of air. In the case of a flowing stream, however, the disk holder should always face downstream in order to prevent direct impingement on the test paper. In all cases, residence time in the suspect atmosphere should be held to a minimum.

The requirement for having a non-color-blind analyst need hardly be mentioned.

TYPICAL OPERATION

The following technique is recommended for most applications of this apparatus. Modifications to fit special needs will usually be concerned only with sample source. Center an indicator disk on the Teflon gasket in the top of the holder and screw in the bottom portion (hand-tight is sufficient). Insert the tubulation into the pump inlet, position the unit in the contaminated air (room, box, stream, duct, etc.), and take a one-stroke sample. The pump is spring-loaded and is operated by squeezing the bellows completely closed, releasing all hand tension, and waiting until the indicating chain is fully extended. (With the 7/16-inch disks, this operation requires approximately 10-12 seconds.) Without removing the disk, and in good light, immediately compare the color of the disk with the calibrated color chart. If the indicated concentration is below 5 ppm on the 100-cc scale, take four additional strokes as rapidly as possible and again compare, using the 500-cc scale. Interpolation between concentrations on both scales is possible and recommended.

The 40 ppm indicated on the 100-cc scale is the minimum concentration required to produce the corresponding color with a 100-cc sample. Neither higher concentrations nor additional strokes will effect an appreciable change. If higher concentrations are suspected, provision must be made for taking smaller samples, or the method must be recalibrated, using larger disks.

CONCLUSION

This technique of rapid grab-sampling of corrosive atmospheres appears to be unique in the realm of acid-gas analysis. The results are quantitative, reproducible, and completely eliminate error due to the time-integrated concentration data that are an unavoidable result of the large samples required for "wet" analysis. The nonspecific nature of the results is not particularly serious if one is mainly concerned with corrosion rather than species. The method should find application in many fields.

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