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EVALUATION OF SORBENTS FOR THE COLLECTION AND ANALYSIS OF TRACE LEVELS OF AIRBORNE VAPORS:
BIS(2-CHLOROETHYL)SULFIDE (MUSTARD), A CASE STUDY

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ABSTRACT

As part of the Department of Health and Human Services's (DHHS's) responsibility for the oversight of safety and health during the destruction of obsolete chemical warfare munitions and agent stockpiles by the Department of Defense (DOD), investigators from the National Institute for Occupational Safety and Health (NIOSH) have conducted research on air monitoring methods that the Department of Defense uses for measuring the workplace and environmental concentrations of chemical warfare agents.

This paper concerns work on part of this research which was aimed at evaluating sorbents for the collection of the blister agent bis(2-chloroethyl)sulfide, known as mustard or HD, from air. Twenty-three sorbents were screened and compared to Tenax, the currently-used sorbent. A screening technique based on the assumption that the sorbents would behave like chromatographic columns was used to select those whose predicted retention volumes at ambient temperature were greater than or equal to that of Tenax. Two promising alternatives were found from the screening experiments. Further testing of those two sorbents, however, uncovered other problems with their use for the collection and recovery of HD which made them unsuitable. The screening technique was shown to be useful for comparison only and did not predict the capacities of sorbents accurately.

INTRODUCTION

As part of the Department of Health and Human Services's (DHHS's) responsibility for the oversight of safety and health during the destruction of obsolete chemical warfare munitions and agent stockpiles by the Department of Defense, Department of the Army, investigators from the National Institute for Occupational Safety and Health (NIOSH) have conducted research on air monitoring methods currently used by the Army for measuring workplace and environmental concentrations of chemical warfare agents.(1) The purpose of this part of the research was to evaluate sorbents for the collection of the blister agent, bis(2-chloroethyl)sulfide, also known as mustard or HD and to compare them to Tenax GC, the porous polymer currently used by the Army to collect HD from the atmosphere for analysis using their Depot Area Air Monitoring System (DAAMS).(2)

The sampling and analytical process for DAAMS consists of (1) collection of the airborne sample on the sorbent in a 6 mm glass tube, (2) transfer to a 3mm glass tube containing smaller amounts of the same sorbent using an external thermal desorber, and (3) thermal desorption in a specially-modified injection port of a gas chromatograph and subsequent analysis using a flame photometric detector. Previous work had shown Tenax to be the best sorbent among those examined for this analysis.(2) The disadvantages of Tenax were: (1) concern about its long-term availability, since it is a synthetic polymer manufactured outside the U.S., (2) its relatively high cost, and (3) Tenax has a lower capacity for HD than the sorbent (Chromosorb 106) used by the Army for nerve agents [O-ethyl S-(2-diisopropylaminoethyl) methyl phosponothiolate] (VX) and isopropyl methylphosphonofluoridate (GB) has for those compounds. Therefore, a study was undertaken to see if any of the readily-available sorbents, which have been used in the industrial hygiene community for air sampling might replace Tenax for this purpose. Those in this category included: Chromosorb 101, 102, 103, 104, 105, 106, 107, and 108 manufactured by Johns-Manville, Denver, CO; Porapak PS, Q, R, and S manufactured by Waters Associates, Milford, MA; Carbotraps B and C distributed by Supelco, Inc., Bellefonte, PA; and XE-340, 347 and 348, and XAD-2 manufactured by Rohm and Haas, Philadelphia, PA. In addition, several experimental carbonaceous sorbents were evaluated, since they held the promise of becoming items of commerce in the near future. This group included Carboxen 563 and 564 and RG2140 B and D distributed by Supelco, Inc., and a proprietary carbonaceous material obtained from SKC, Inc., Eighty Four, PA.

The replacement sorbent, ideally, would have the following attributes: (1) it should have a larger capacity for HD than Tenax, and (2) HD should be recoverable from the sorbent in high yield by thermal desorption at an injector temperature of 250°C., the temperature used in the final desorption step of the DAAMS tube analysis.

MATERIALS AND METHODS

Equipment

A Hewlett-Packard 5890A gas chromatograph (gc) equipped with a flame photometric detector in the sulfur mode was used throughout this study. It was configured in one of two ways:

(1) For sorbent evaluation: A system was assembled to enable the rapid exchange of sorbents for evaluation (Figure 1).(4) It consisted of a three-part glass assembly of 6mm o.d. silanized Pyrex tubing joined together by bored-out 1/4 inch stainless steel Swagelok fittings and graphite ferrules. The three glass pieces formed a U-tube consisting of an injection port tube, a detector port tube and a sample tube.

The sorbent was packed into the sample tube and then cleaned by heating overnight in the oven of the gas chromatograph under a stream of helium

carrier gas at the maximum isothermal temperature for the sorbent, or 250°C whichever was lower.

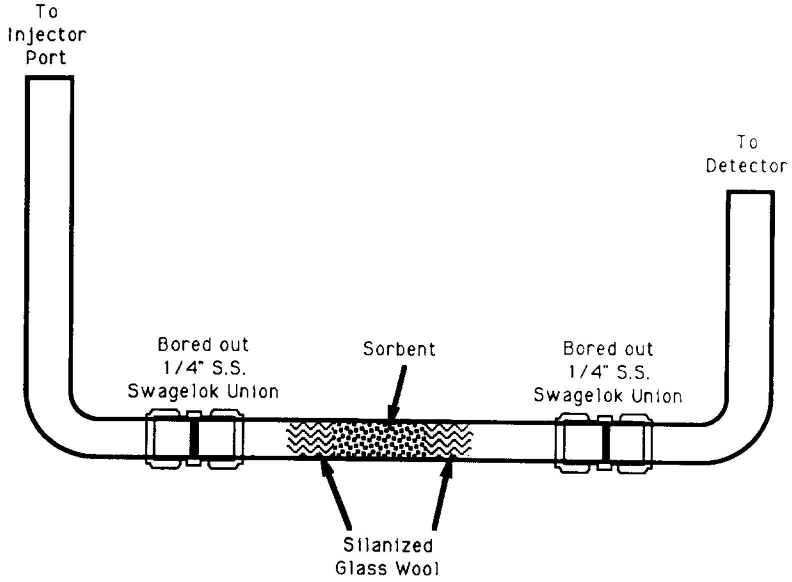

Figure 1. Sorbent Evaluation System

(2) For recovery measurements from DAAMS tubes: It was fitted with the thermal desorption injector port insert specially developed for DAAMS tubes by Southern Research, Inc. of Birmingham, AL,(3) from whom it was purchased. The columns used were: (1) a DB210, 15m megabore column of 1.0 μm film thickness, or (2) a Carbowax, 15m megabore column of 1.2 μm film thickness. The injector temperature was 250°C, and the detector temperature was 260°C. Column temperatures were 90°C and 150°C for columns 1 and 2 respectively. Flow rates of combustion gases to the detector were 100 mL/min air ±5%, and 62 mL/min hydrogen ±5%. Carrier flow was 20 ml/min ±10% of helium. Integration was performed using either a Hewlett-Packard 3393A integrator or a Nelson Analytical 900 series interface and PC integrator software.

Sorbent Screening

A screening technique which has been used previously to obtain physico-chemical parameters of sorbents was used to search for a replacement sorbent.(4-8) Mathematically, the relationship which holds for most sorbent-sorbate combinations is: the logarithm of the retention volume (RV) is proportional to the inverse of the absolute temperature,T, or:

$$\mathrm{Ln}(RV) \propto 1/T \quad (1)$$

In practice, a short chromatographic column containing the sorbent to be tested was prepared; the retention time of the sorbate on that column was then measured at various temperatures. Since the sorbate will elute from the short column as a measurable peak only over a small range of temperatures, the slope and intercept of the line generated from plotting the data according to equation 1 over that short range were found. The retention volume at ambient temperature was obtained by extrapolation. The retention volume is calculated by multiplying the retention time found by the extrapolation technique by the flow rate of the carrier gas through the column. By comparing the predicted retention volumes for various sorbents to that of Tenax, it should be possible to select for further screening a small number of sorbents whose predicted retention volumes were greater. It was expected that the extrapolation would likely not produce an exact value for the retention volume, because of the uncertainty in the extrapolation process; the logarithmic nature of the relationship, which tends to exagerate the extrapolation errors; and because what is predicted is the retention volume at the peak maximum, which is not identical to that at breakthrough. At ambient temperature, breakthrough is virtually certain to produce an attenuated peak shape whose maximum, if it were possible to measure it, would occur long after breakthrough begins. Thus retention volume is likely to be over-estimated by this predictive scheme. Using this relationship, however, it should be possible to extrapolate to any temperature of interest, which may, for example, be valuable if the sorbent is used to collect unburned starting material in stack effluent, as is currently being proposed at incineration sites. In addition, by comparison of the area under the peak obtained from the test sorbents with that obtained using Tenax, it would be possible to estimate recovery from the test sorbent. Also, artifactual peaks present in the chromatograms from the test sorbents are an indication of decomposition of the sorbate.

Reagents

The sorbate, in this case HD, was supplied by the Army as a dilute solution in hexane (5.37 mg/mL), lot# HD/N-Hex-8047-CTF-DIL. Dilutions were made to obtain standard solutions in the range of 2-50 μg/mL. At the Surgeon General's recommended TWA level of 3 $\mu g/m^3$(9) using the Army's DAAMS tube sampling time of two hours and flow rate of 200 mL/min, 72 ng of mustard would be collected. This amount saturated the flame photometric detector. Therefore, more dilute solutions were made and used in the tests; the amount injected corresponded to that which would be collected using the Army's time and flow rate conditions at about 5% of the TWA level, or about 4 ng of HD per injection. Additionally, by using levels well below the TWA, the testing procedure was adjudged more likely to detect problems which might go undetected at the higher levels.

Screening Procedure

Any sorbent which produced a high background at 200°C was adjudged unsuitable. During conditioning, only the injector and sample tube parts of the Sorbent Evaluation System in Figure 1 were connected to the carrier gas. After conditioning, the gas chromatograph was allowed to cool to room temperature, the detector piece was attached to the assembly to form the U-tube and inserted in the flame photometric detector of the gc. The assembly was then heated, and injections were then made through a septum on top of the heated injection port, directly into the injector tube assembly.

The retention time of the eluted peaks as a function of column temperature for at least four temperatures was measured and recorded. Data consisting of the retention times (rt), which were corrected for the transit time of a non-retained species and normalized to a 25mg sorbent bed, versus the inverse of the absolute temperature multiplied by 1000 for convenience (1000/T), was used to calculate the regression parameters of slope, m (having units of minutes deg.K); intercept, b, (a unitless parameter corresponding to the logarithm of the retention time in minutes of the sorbate on the sorbent at infinite temperature); and correlation coefficient, r. (See Tables 1 and 2). Half mustard (2-chloroethyl ethylsulfide) was used as a surrogate to do a preliminary screening of the sorbents. The structures for half mustard and mustard are:

$ClCH_2CH_2SCH_2CH_3$	Half mustard
$ClCH_2CH_2SCH_2CH_2Cl$	Mustard

The two compounds differ only by the substitution of a chlorine for a hydrogen. Those sorbents which had predicted retention volumes as large or larger than that of Tenax for half mustard were selected for further testing with HD.

Recovery Studies - Liquid Spike

Based on the data obtained in the screening tests done on mustard, Chromosorb 107 and Carbotrap B were selected for further testing. Therefore, DAAMS transfer tubes containing Tenax and those two sorbents were ordered from the Army's supplier of sorbent tubes, CMS Research Corp., of Birmingham, AL. These transfer tubes were thermally cleaned, then spiked with HD in hexane and thermally desorbed in the standard Army manner.(3) Recoveries of HD were measured and compared to those obtained with the Tenax.

Recovery Studies - Liquid Spike/Vapor Transfer

Tenax, Carbotrap B and Chromosorb 107 DAAMS sample and transfer tubes of the standard Army type(3) were obtained from the same Army supplier as above. These tubes were cleaned by heating at 250°C overnight in a gas chromatograph oven with helium carrier gas flow. The cleaned sorbent tubes were spiked with HD in hexane at the 4.26 ng/tube level. They were then attached to transfer tubes containing the same sorbent by means of a 1/4 inch to 1/8 inch Swagelok reducing union and desorbed by placing the sampling tubes in a heated block at 250°C while air was drawn through the combined tube assembly. The transfer tubes were then thermally desorbed in the gc using the standard Army DAAMS tube method(3) and the amount recovered compared with the amount originally spiked.

Breakthrough Determination

Each of the DAAMS sample tubes to be evaluated was placed in-line with a concentration of 3 ng/L HD in air. The effluent concentration from the sorbent tube was continuously sampled by a continous-sampling automated air sampling device used to detect airborne chemical agent at demilitarization sites. Air is sampled by passing through a concentrator tube for 6.5 minutes; then the tube is thermally desorbed onto a gc column with a flame-photometric detector which detects and quantitates the presence of HD. Breakthrough occurred when HD was detected. These tests were done under both low (10%) and high (90%) relative humidity conditions as measured by a Vaisala HMI 32 digital humidity monitor.

RESULTS AND DISCUSSION

Sorbent Screening

The results of the half mustard study are contained in Table 1. The data show that over the temperature ranges studied, Equation (1) holds quite well, based on the high correlation coefficient, r, obtained for nearly all the sorbents studied. Several of the more promising sorbents were examined at a lower weight of sorbent, to more closely approach sorbent tube conditions. One would expect a small increase in the predicted capacity at ambient temperature with a decrease in bed length since the smaller sorbent bed will not contain as many theoretical plates and therefore the peak will be attenuated, and the peak maximum will occur at longer than previously predicted time.

The expected small increase in capacity with decreasing weight of sorbent was observed in the cases of Porapak S, Chromosorb 106, and Chromosorb 107, but not in the case of Carbotrap B, which evinced a large loss in capacity. This sort of behavior indicated that the sorbent was not acting in the expected fashion. Nevertheless, it was decided to continue the evaluation of this sorbent, since it was not clear whether the observed phenomenon was sorbent or sorbate related. Based on the half mustard screening test results, those sorbents having predicted breakthrough capacities greater than or equal to that of Tenax, namely Chromosorb 105, Chromosorb 106, Chromosorb 107, Chromosorb 108, Porapak S, and Carbotrap B, were selected for further testing with HD. The data from these experiments are summarized in Table 2. Chromosorb 105 and 106 and Porapak S gave evidence of irreversible processes as evidenced by small (compared to Tenax) and/or artifactual peaks and were, therefore, eliminated from further consideration. Chromosorb 107 looked quite promising and Carbotrap B continued to present evidence that it was behaving in an unexpected way, by showing some irreversible behavior at larger bed length but not at the lower level.

TABLE 1

Sorbent Parameters - Half Mustard[a]

Sorbent	Slope	Intercept	r	Wt.	Capacity	Comments
Carbotrap B	8.06	-16.6	.999	400	141	
Carbotrap B	6.76	-16.1	.999	100	6.66	
XAD-2	7.57	-16.1	1.00	400	26.4	200°Ct_{max}
Porapak PS	6.92	-15.7	.999	300	5.72	
Porapak Q	7.34	-14.9	.999	400	40.0	high background at 250°C and 2nd pk
Porapak R	7.44	-15.6	.998	300	37.3	
Porapak S	7.70	-15.7	1.00	400	61.5	240°C t_{max}
Porapak S	7.81	-18.0	.999	50	71.8	
Chromosorb 101	6.03	-13.7	.989	300	2.02	
Chromosorb 102	7.75	-16.3	.999	400	40.0	
Chromosorb 103	6.08	-13.7	.988	400	1.80	small peak
Chromosorb 104	8.18	-17.8	.999	400	38.7	225°C t_{max}, small peaks
Chromosorb 105	8.41	-18.1	.996	400	62.9	small peaks
Chromosorb 106	8.02	-15.5	.999	400	224	
Chromosorb 106	8.10	-17.8	1.00	50	236	
Chromosorb 107	8.75	-17.8	.985	400	271	
Chromosorb 107	8.48	-18.7	1.00	50	351	
Chromosorb 108	8.11	-17.6	1.00	400	36.5	
Tenax	8.73	-20.8	.993	100	50.4	
Tenax	9.26	-23.0	1.00	50	68.2	
Carbotrap C						No capacity
XE-340						Unusable - high bkgr
XE-347						" " "
XE-348						" " "
Carboxen 563[b]						" " "
Carboxen 564[b]						" " "
RG 2140 B[b]						" " "
RG 2140 D[b]						" " "
Proprietary carbon[c]						" " "

[a] Slope (units: 10^{-3} min K), intercept, and r the correlation coefficient, were calculated from the regression line of the data points. Wt. is the mass in mg. of the sorbent in the sorbent tube. Capacity is the number of liters of inert gas, predicted from the regression line, which would pass through 25 mg. of sorbent at 20 deg C before the peak maximum would appear.

[b] Experimental carbonaceous sorbent from Supelco, Inc.
[c] " " " " SKC Corp.

TABLE 2

Sorbent Parameters - Mustard (HD)[a]

Sorbent	Slope	Intercept	r	Wt.	Capacity	Comments
Tenax	10.6	-23.3	1.00	150	$1.63x10^3$	
Tenax	11.6	-26.7	1.00	50	4.96 "	
Carbotrap B	10.2	-19.5	.999	400	6.98 "	small peak
Carbotrap B	9.12	-18.2	.998	150	1.71 "	
Chromosorb 105	8.94	-17.2	.999	400	920	small peak
Chromosorb 106						2peaks -decomposition
Chromosorb 107	10.3	-19.2	.999	400	$1.33x10^4$	
Chromosorb 107	11.1	-12.9	1.00	50	4.02 "	
Porapak S						2 peaks -decomposition

[a] Slope (units: 10^{-3} min K), intercept, and r the correlation coefficient, were calculated from the regression line of the data points. Wt. is the mass in mg. of the sorbent in the sorbent tube. Capacity is the number of liters of inert gas, predicted from the regression line, which would pass through 25 mg of sorbent at 20 deg C before the peak maximum would appear.

Recovery Studies - Liquid Spike

A problem with Chromosorb 107 became immediately apparent. The first time the tubes were spiked and desorbed, the peak area was quite small. The second time that this process was repeated on the same tube, done as soon as the tube cooled down, gave a normal-sized peak. This phenomenon was noted for all Chromosorb 107 tubes and was reproducible. One possible explanation for the observed effect is the production, on standing, of a species which reacts irreversibly with HD. The process may involve a reaction of the sorbent with air or moisture or light or a combination of those. Regardless of the specific reaction involved, the sorbent becomes unusable for the purpose of collecting HD, since the same process which occurs on standing will occur while samples are being collected. Results of a recovery study on the other two sorbents are presented in Table 3.

Table 3

Recovery of HD from Liquid-spiked Transfer Tubes

Peak Areas in Arbitrary Integrator Units

	Tenax	Carbotrap B
	5070	4830
	5335	4874
	4290	4471
	5790	4471
	5516	4763
	5539	4347
	5203	4166
	5129	4590
	4187	4718
	3890	4660
	4240	4383
	5685	4067
Averages:	4990 ± 13.2%	4534 ± 5.9%

The average recovery for the Carbotrap B tubes was 4534/4990, or 90.8% of the Tenax recovery. This difference was significant at the 5% level using a two-tailed t test.

To see whether this difference in recovery was due to an irreversible loss on Carbotrap B or whether it might be related to differences in the shape of the desorption curve, the experiment was rerun using a temperature programmed protocol, holding the temperature of the gc oven at a low temperature for two minutes and then raising the temperature rapidly to elute the HD collected on the cold column. Using this technique, the effects of tailing of the HD from the sorbent during thermal desorption should disappear. Indeed, the finding was that for a set of 12 analyses for each type of tube, the integrated areas were virtually identical, showing irreversible losses were not occurring, and strongly supporting the idea that the shape of the thermal desorption curve from the transfer tube was the cause of the initially-observed incomplete recovery.

Recovery Studies - Liquid Spike/Vapor Transfer

When the initial experiments were run using the DAAMS sampling tubes obtained from CMS Research, Inc., the recovery from the Carbotrap B tubes was only about 50% of that obtained from the Tenax tubes. Because the tubes were filled to the same bed depth and because of the difference in density between Carbotrap B and Tenax, the weight of sorbent in the tubes used in the experiment averaged about 90 mg in the case of Carbotrap and about 30 mg for the Tenax tubes. Having observed a difference in recovery for different weights of Carbotrap B in the screening experiments, the experiment was rerun using less Carbotrap. Tubes were prepared in the lab containing 40 mg of Carbotrap B in the same silanized Pyrex tubes which had been used as sorbent tubes in the screening experiment. Results from these recovery experiments are presented in Table 4. There was no difference in recovery between the sorbents (2-tailed t test) under these conditions.

Table 4

Recovery of HD from Liquid-spiked DAAMS Sampling Tubes

Following Thermal Desorption from Transfer Tubes

(Arbitrary Integrator Units)

	Tenax	Carbotrap B
	5055	4706
	4847	5043
	4849	5586
	5343	5031
	4608	4938
	4825	4815
	4048	5333
	5436	4428
Average:	4876 ± 8.92%	4860 ± 10.1%

Breakthrough Experiments

Results of breakthrough experiments on Tenax tubes purchased from CMS and 40 mg Carbotrap B tubes prepared as described above in the laboratory were as follows:

Table 5

Approximate Breakthrough Volume (Liters) For HD

	Tenax	Carbotrap B
10% RH	307	197
90% RH	165	33.6

Clearly the capacity for HD is greater on Tenax than on Carbotrap B under both conditions. Furthermore, for Tenax the per cent decrease in capacity on going from 10 to 90% RH was about 50%, while for Carbotrap B it was about 80%. Comparing the predicted capacity values in Table 2 for a 150 mg bed with the 10% RH breakthrough volumes in Table 5 reveals that Tenax had about 20% of its predicted value, and Carbotrap B about 10%. Thus, for this combination of sorbents and sorbate at least, equation (1) is useful only for screening purposes and does not accurately predict sorbent capacity. In addition, the difficulties encountered with the Chromosorb 107 and Carbotrap B in later experiments reinforces the necessity for further testing of sorbents even though chromatographic-type experiments may indicate that they have adequate capacity.

CONCLUSIONS

No sorbent was found in this study which surpassed the capacity and recovery characteristics of the Army's currently-used material, Tenax. Carbotrap B has less capacity under both high and low humidity conditions than does Tenax. Furthermore, the per cent loss of capacity in going from a dry to a wet condition is much larger for Carbotrap B than it is for Tenax.

For reasons probably related to the differences between the chromatographic experiment and collection of a "real world" sample, it was not possible to use retention volume vs. temperature data to predict breakthrough volume of a sorbent bed accurately. This type of experimental data is, however, probably useful as a screening technique in which (1) certain sorbents can be eliminated if irreversible behavior is noted, and (2) those sobents having large capacities for the tested vapor can be identified and further tested.

The relationship between the log of the retention volume and the inverse of the temperature, which in many cases governs sorbent-sorbate chromatogaphic behavior, does not accurately predict sorbent capacity for small beds of the size typically used for the collection of analytes from air.

DISCLAIMER

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

REFERENCES

1. Interagency Agreement between Centers for Disease Control and Department of Defense, Department of the Army, dated 10/26/86, Contract No. J48658.

2. Smith, J.E., Jr. and W.K. Fowler: "Analytical Methods Development, Vol. 1- Experimental Studies, Final Report", Contract DAAK11-82-C-0162," US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Grounds, MD 21010, December 1985, pp. 106-152.

3. Smith, Jr., J.E. and W.K. Fowler,: "Analytical Methods Development, Vol. 1- Experimental Studies, Final Report", Contract DAAK11-82-C-0162," US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Grounds, MD 21010, December 1985, Appendix A, Apparatus and Procedures for the Depot Area Air Monitoring System (DAAMS) (December 1985).

4. Betz, W.R., et al.: "Characterization of Carbon Molecular Sieves and Activated Charcoal for Use in Airborne Contaminant Sampling," Am Ind Hyg Assoc J 50(4):181 (1989).

5. Pellizzari, E.D., et al.: "Collection and Analysis ofTrace Organic Vapor Pollutants in Ambient Atmospheres. The Performance of a Tenax GC Cartridge Sampler for Hazardous Vapor," Anal Letts, 9(1):45-63 (1976).

6. Lunsford, A.L. and P. Fey: "Backup Data Report for P&CAM 301, Dimethyl Sulfate," NIOSH, unpublished (December 29,1978).

7. Hawkes, St.J.: "Predicting Retention Data Using the Slope of the Log Adjusted Retention Time Vs. Carbon Number Plot for n-Alkanes," Chromatogaphia 25(4):313-318 (1988).

8. Laub, R.J. and R.L. Pecsok: Physico-chemical Applications of Gas Chromatography, Wiley Interscience, New York, pp. 110-111 (1978).

9. Federal Register, Vol. 53, #50, p.8504-8507 (March 15, 1988).

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