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Project Summary

Response of Portable VOC Analyzers to Chemical Mixtures

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The report gives the responses of two types of portable VOC analyzers (Century Systems OVA-108 and Bacharach TLV Sniffer), calibrated with methane and used to measure a variety of chemical vapor mixtures. Instrument response data for both binary and ternary mixtures of selected chemicals are presented. Various empirical models were evaluated to determine an appropriate method of estimating mixture concentration based on instrument response. The evaluation concluded that the instrument response for a mixture falls between the responses expected for the pure compounds in the mixture. Thus, an interpolation or weighted average model can be used to predict the response for mixtures based on known responses for individual chemicals. Both linear and logarithmic weighted average models are applied to the data and presented with estimates of accuracy. In general, these models predicted the instrument response to within 30 percent of the observed value.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Portable VOC (Volatile Organic Compound) analyzers have been widely used in the identification of fugitive emission sources, a process commonly called "screening." Screening is important both in research to develop emission factors and in proposed regulatory monitoring of fugitive emissions. While these VOC analyzers will respond to most organic vapors, they respond with varying sensitivity to different chemical species.

Previous to the present study, Radian Corporation performed a laboratory evaluation of the response characteristics of two common VOC analyzers (the Century Systems OVA-108 and the J.W. Bacharach TLV Sniffer) to a large variety of individual organic compounds in air. The results of this previous EPA-funded study are available in two reports EPA-600/2-81-002 (NTIS PB81 136194) and EPA-600/2-81-051.

This summary presents the results of testing in the area of chemical mixtures. The data base reported here includes response data on nine binary chemical combinations of acetic acid, acetone, chloroform, cyclohexane, benzene, methanol, and methyl ethyl ketone plus one ternary combination.

The results of these analyses show that the response to a binary chemical mixture falls between the responses of the two individual chemicals at the total concentration of the mixture. This indicates that synergistic effects are weak and suggests that some form of interpolation or weighted average can be used to predict the response of the mixtures based on individual chemical response characteristics.

Computation Methods

This section describes and discusses methods for estimating concentrations when VOC instrument responses are known. The fractional composition of the detected vapors must also be known. Computed and graphical estimates are discussed.

In general, the VOC instrument response to a mixture of compounds is intermediate to the individual responses to each one of them at the same total concentration. This effect may be approximated by a weighted average of the responses (or linear interpolation in the case of two chemicals). An estimate of the weighted average response is:

$$R_A = \sum_i p_i a_i C_T^{b_i} e^{\frac{1}{2}s_i^2} \qquad (1)$$

where

R_A = the estimated weighted average response,

P_i = the fraction of the mixture total concentration accounted for by compound i ($P_i = C_i/C_T$),

a_i = exp(A) with "A" from Brown, *et al.* (1980)* for component i,

b_i = coefficient "B" from Brown, et al. (1980) for component i,

s_i = parameters "SE" from Brown *et al.* (1980) for component i,

$C_T = \sum C_i$, the total concentration, and

C_i = the concentration in the mixture of compound i.

The coefficients A, B, and SE can be found in Tables 5-169 and 5-170 of Brown, *et al.* (1980) for selected compounds.

The above discussion involves the prediction of an instrument response when the actual concentration of mixture components is known. In a practical situation, the reverse is the case: the response is observed and it is desired to estimate the concentration of the constituents. Basically, this cannot be done without some additional information. The compound identification of the constituents must be known. If the constituent proportions are also known, the total concentration can be computed assuming the above model is correct. The total concentration (C_T) is estimated by solving Equation (1).

Equation (1) cannot be solved explicitly for total concentration. An iterative solution is required. This can be done using the Newton-Rhapson method. Letting

$$f(C_T) = \sum_i p_i a_i C_T^{b_i} e^{\frac{1}{2}s_i^2} - R \qquad (2)$$

where R is the observed instrument response, and

$$f'(C_T) = \sum_i p_i b_i a_i C_T^{b_i - 1} e^{\frac{1}{2}s_i^2}, \qquad (3)$$

then the iteration formula is:

$$C_{i+1} = C_i - f(C_i)/f'(C_i). \qquad (4)$$

A reasonable starting value C_o is R, the observed instrument response.

Alternatively, a weighted logarithmic average may be used. In this case:

$$\log(R_L) = \sum_i p_i \left[\log a_i + \tfrac{1}{2}s_i^2 + b_i \log C_T\right] \qquad (5)$$

where R_L is the estimated instrument response using a weighted logarithmic average and logarithms are to base e.

In contrast to the previously given weighted arithmetic average model, Equation (1), this weighted logarithmic average model, Equation (5) has an explicit solution for actual total concentration:

$$\log C_T = \frac{\log R - \sum p_i (\log a_i + \frac{1}{2} s_i^2)}{\sum p_i b_i} \qquad (6)$$

For binary mixtures, the solutions are as follows. The arithmetic weighted average iteration formula is:

$$C_{i+1} = C_i - f(C_i)/f'(C_i) \qquad (7)$$

where

$$f(C_T) = p_1 a_1 C_T^{b_1} e^{\frac{1}{2}s_1^2} + p_2 a_2 C_T^{b_2} e^{\frac{1}{2}s_2^2} - R,$$

$$f'(C_T) = p_1 b_1 a_1 C_T^{b_1 - 1} e^{\frac{1}{2}s_1} + p_2 b_2 a_2 C_T^{b_2 - 1} e^{\frac{1}{2}s_2^2},$$

and

C_o = R or another suitable starting value.

The logarithmic weighted average solution is:

$$\log C_T = \frac{\log R - p_1(\log a_1 + \frac{1}{2}s_1^2) - p_2(\log a_2 + \frac{1}{2}s_2^2)}{p_1 b_1 + p_2 b_2} \qquad (8)$$

Results

The models discussed above predict the mixture response by weighted average or linear interpolation between the response of two pure chemicals on either an arithmetic or a logarithmic scale. This "weighted average" model is readily extendable to three or more compounds. A summary of the response data and the precision of these two models is given in Table 1. Neither the arithmetic nor logarithmic scale model shows any clear advantage when applied over the entire data set. However, the logarithmic model gives much poorer estimates than the arithmetic model in some cases. Both models are able to predict mixture response to within about ±30 percent of the observed value, which is about as good as the single chemical data on which the models are based. There is some advantage to the logarithmic scale model in that it has a discrete solution, while the arithmetic scale model must be solved iteratively or graphically.

*In report EPA-600/2-81-002 (NTIS PB81-136194)

Table 1. *Comparison of Percent Error for Arithmetic and Logarithmic Weighted Average Models for Mixtures*

	Average Percent Error of Model Prediction			
	OVA		TLV	
Compound Mixtures	Arithmetic	Logarithmic	Arithmetic	Logarithmic
Acetic Acid and Chloroform	25	20	-83	-88
Acetic Acid and Cyclohexane	31	11	4	-37
Acetic Acid and Acetone	33	27	-3	-28
Acetone and Chloroform	39	17	-21	-80
Acetone and Cyclohexane	31	28	7	3
Benzene and Methyl Ethyl Ketone	-9	19	9	9
Benzene and Methanol	-1	-121	10	8
Chloroform and Cyclohexane	29	-5	-13	-90
Methanol and Methyl Ethyl Ketone	-16	-87	12	9
Benzene, Methanol, and Methyl Ethyl Ketone	-9	-50	12	9

Compound	Response Factor*		Compound	Response Factor*	
	OVA	TLV		OVA	TLV
Acetic Acid	1.64	15.60	Cyclohexane	0.47	0.70
Acetone	0.80	1.22	Methanol	4.39	2.01
Benzene	0.29	1.07	Methyl Ethyl Ketone	0.64	1.12
Chloroform	9.28	**			

*Ratio of actual concentration to instrument response at 10,000 ppmv response (EPA-600/2-81-051).
**A 10,000 ppmv response to chloroform with TLV is not achievable.

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The complete report, entitled "Response of Portable VOC Analyzers to Chemical Mixtures," (Order No. PB 81-234 262; Cost: $8.00, subject to change) will be available only from:
National Technical Information Service
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