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Project Summary

A Gravimetric Technique for the Preparation of Accurate Trace Organic Gas Standards

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An accurate procedure based on microgravimetry has been used for the preparation of volatile, hazardous organic chemicals in a nitrogen matrix in pressurized gas cylinders at analyte concentrations ranging from 10 ppb to 10 ppm, by mole. In this technique, the organics of interest are individually weighed into separate glass capillary tubes using a microanalytical balance. The tubes are sealed, and subsequently broken in a fixed line connected to an evacuated cylinder. A known weight of pre-analyzed matrix gas (nitrogen) is then used to pressurize the cylinder, and the concentrations of the organics are calculated on a molar basis relative to the number of moles of the matrix gas.

A number of these gravimetric primary mixtures have been prepared and analytically intercompared using gas chromatography (GC) with flame ionization detection (FID). Excellent agreement has been found between analyte concentration values prepared gravimetrically and concentration values determined by analysis.

This paper will focus on a description of the microgravimetric technique and the analytical system, the estimation of specific uncertainties associated with the preparation of these mixtures, and how these uncertainties are used to assign a net uncertainty to the final analyte concentration. Particular attention is given to mixtures at the 10 to 150 ppb level. A brief description of how the overall network of gravimetric primary standards provides long term, consistent data quality for trace organic gas mixtures is included.

This Project Summary was developed by EPA's Environmental Monitoring Systems 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).

Discussion

Compressed gas standards of multicomponent volatile toxic organic compounds in the low part-per-billion (PPB) range are prepared by a special gravimetric procedure developed at the National Bureau of Standards using extreme caution. By this procedure, the targeted concentrations are obtained by quantitatively mixing known weights of each of the organics with a known weight of pure nitrogen matrix gas in a new precleaned aluminum cylinder, with the resulting concentrations of the organics expressed in nanomoles/mole (ppb) of the total mixture.

A brief description of the procedure follows: A glass capillary tube (approximately 20 mm long by 1.6 mm OD), for which one end had been sealed and the other had been drawn to a fine open tip, is weighed empty. The desired organic is drawn into the tube by air displacement, following which the tube is centrifuged to force the organic liquid to the sealed end of the tube. The tube is then sealed and weighed to obtain the weight of the organic. The tube is then inserted into a teflon sleeve attached to a tared, evaluated aluminum cylinder. The valve of the cylinder is slightly opened and the capiliary tube is cracked open inside the teflon sleeve and the organic is trans-

ferred into the cylinder with mild heating from a hot-air gun. This process is repeated for each organic added to the desired mixture, following which the cylinder is pressurized with dry, clean nitrogen and weighed.

A series of six standard five-component organic mixtures were prepared in this manner at concentrations ranging from about 5-150 ppb by mole to ascertain the linearity of the overall concentration range and the feasibility of preparing and analyzing such mixtures. The five components are identified in Table 1. The standards were analyzed by gas chromatography using a flame-ionization detector (FID), with the detector response plotted vs. gravimetric concentration in a linear regression fit. The concentrations predicted from the linear regression plot agreed well with the gravimetric concentrations, indicating the presence of negligible random errors in the preparation of these standards. The mean of the differences for any one fit (e.g., benzene) (Table 1) represents the imprecision of the gravimetric preparation for that organic.

The total uncertainty of the concentration of any of the organics at the 95% confidence level is determined by two times the square root of the sums of the squares of the imprecision of analysis (obtained by replicate analyses) and the imprecision of gravimetric preparation. While the total uncertainties of the concentrations of the organics is quite acceptable for these low concentrations, the total uncertainties of the concentrations for the halogenated organics present in these mixtures could be further reduced by the use of an electron capture detector (rather than an FID) due to the markedly greater signal obtainable for halogonated organics with this detector. To illustrate: the total uncertainty at 95% confidence for chloroform when analyzed by FID was 10%, but was reduced to 2% using an electron capture detector.

Gravimetrically prepared standards encompassing more than 30 volatile organic compounds (all designated by EPA) have been prepared under this program, representing a systematic network of overlapping concentrations ranging from the low part-per-million level to the low-ppb level. Such standards have typically shown excellent long-term stability at these low concentrations over several years of reanalyses. Stable concentrations of some of these organics have been gravimetrically prepared to as low as one ppb and NBS-traceable standards have been provided to EPA that contain as many as nine organic compounds in the same mixture. Work currently is underway to prepare a mixture at the 10 ppb level containing in excess of 15 volatile organic compounds. The standard output of this program currently serves to provide the basis for data quality assurance and traceability of national ambient air and hazardous waste incineration monitoring efforts.

Table 1. *Comparison of Gravimetric and Analyzed Concentrations*

Component	Cylinder	Gravimetric Conc., ppb	Analyzed Conc., ppb		Percent Difference[c]
Benzene	AAL-11133	99.9	99.9		0
	CAL-7493	46.8	46.7		-0.2
	CAL-8746	38.2	39.0		+2.1
	AAL-12029	37.0	36.3		-1.9
	AAL-7001	15.1	---[a]		---
	AAL-7009	7.6	7.56		-0.5
				$\bar{x}$ =	0.9
Vinyl chloride	AAL-11133	152	152		0
	CAL-7493	86.0	85.1		-1.0
	CAL-8746	---[b]	23.0		---
	AAL-12029	24.5	24.8		+1.2
	AAL-7001	20.6	20.7		+0.5
	AAL-7009	5.54	5.54		0
				$\bar{x}$ =	0.5
Chloroform	AAL-11133	101	101		0
	CAL-8746	27.3	28.2		+3.3
	AAL-7001	19.9	19.9		0
	CAL-7493	19.8	20.5		+3.5
	AAL-12029	16.1	15.8		-1.9
	AAL-7009	4.68	4.59		-1.9
				$\bar{x}$ =	1.8
Carbon tetrachloride	AAL-11133	107	107		0
	CAL-7493	35.1	32.5		-7.4
	CAL-8746	25.9	---[a]		---
	AAL-12029	23.5	23.6		+0.4
	AAL-7001	16.2	---[a]		---
	AAL-7009	6.76	6.68		-1.2
				$\bar{x}$ =	2.2
Tetrachloroethylene	AAL-11133	132	132		0
	CAL-7493	27.6	27.7		+0.4
	AAL-12029	13.6	13.7		+0.7
	AAL-7001	13.3	12.2		-8.3
	CAL-8746	10.3	11.2		+8.7
	AAL-7009	3.71	3.57		-3.8
				$\bar{x}$ =	3.6

[a] *Particular organic showed interference by a trace impurity in the chromatogram.*
[b] *Analysis gave a reliable, consistent value which was different from the gravimetric value.*
[c] *Percent difference calculated from: [Analyzed conc. - gravimetric conc.] x 100, divided by gravimetric conc.; the mean percent differences ($\bar{x}$) represent the imprecision of the concentration.*

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***Howard Crist** is the EPA Project Officer (see below).*
The complete report, entitled "A Gravimetric Technique for the Preparation of Accurate Trace Organic Gas Standards," (Order No. PB 87-145 736/AS; Cost: $9.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
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