Internal standards: A source of analytical bias for volatile organic analyte determinations

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Abstract

The use of internal standards in the determination of volatile organic compounds as described in SW-846 Method 8260C introduces a potential for bias in results once the internal standards (ISTDs) are added to a sample for analysis. The bias is relative to the dissimilarity between the analyte and internal standard physical properties that influence how easily analytes are separated from a matrix and concentrated during analysis.

Method 5032 is a vacuum distillation procedure for extracting analytes from a sample for use with Method 8260C. Vacuum distillation is also incorporated within another GC/MS analytical procedure, Method 8261A. Method 8260C/5032 and Method 8261A are experimentally identical however Method 8261A uses internal standards differently by relating the recovery of each compound to its boiling point and relative volatility. By processing each analysis (water, soil, and biota) using both Method 8260C and Method 8261A, the two approaches are compared on the basis of analyte bias and the failure rate of the quality controls.

Analytes were grouped by how similar their boiling points and natural log of their relative volatilities (lnRVs) were to their Method 8260C recommended ISTDs. For the most similar analytes, the Method 8260C determinations yielded an average bias less than 10% and a failure to meet calibration criteria less than 7%. However, as the difference between analyte and ISTD became greater the bias increased to over 40% (matrix dependent) and its calibration failure rate approached 70%. In comparison, when the Method 8260C data were reprocessed as Method 8261A determinations, this trend for groupings was minimized with biases increasing from 6 to only 20% and the calibration failure rate went from 0 to 15%.

Key words: volatile organic compounds, internal standards, bias, biota, soil, water, analyses

1. Introduction

Volatile organic compounds (VOCs) make up a major group of compounds routinely monitored as environmental contaminants. RCRA SW-846 Method 8260C is the determinative protocol of choice with a pre-concentration protocol such as headspace (Method 5021) or purge-and-trap (Method 5030C) [1]. There are investigations addressing measurement uncertainty as analytical [2, 3], sampling and sub-sampling errors [4], and their comparative importance [5]; however, for VOC determinations there is a

potential bias rarely addressed. That is, the dissimilarity between analytes and their internal standards (ISTDs) can result in quite different behavior during analyses.

Method 8260C describes the use of GC/MS for quantification of analytes with guidance for quality control. The method uses internal standards that are added to samples to compensate for changes in responses between a calibration standard and a sample by simply applying the relative change in internal standard response to the analyte response. This internal standard approach has been part of EPA methods for determining VOCs since being included in Method 624 for VOCs in drinking water [6]. Additional analytes, internal standards, and surrogates have since been added and now RCRA Method 8260C is applied to a wide range of analytes and for a plethora of matrices. Quality controls have been included in the method to insure that the behavior of analytes is uniform (calibration and continuing calibration criteria) and "matrix effects" are minimal (limits for relative response of internal standards and surrogate recoveries). When results deviate from these limitations, the results are considered unreliable and thus qualified as estimated values.

Method 8261A is another SW-846 method that can be used to determine VOCs [7]. Unlike Method 8260C, Method 8261A includes both vacuum distillation pre-concentration and quantitation as a single method. The vacuum distillation pre-concentration procedure described in Method 8261A is also described in Method 5032 for use with Method 8260C. Method 8261A and Methods 8260C/5032 are experimentally identical, except how the internal standards are used. Rather than relating the response of an analyte to its recommended internal standard, Method 8261A relates the response of an analyte to its boiling point and water-to-air partitioning during distillation (relative volatility). The responses of internal standards are used to solve an algorithm that then is used to determine the recovery of each analyte as a function of the analyte's boiling point and relative volatility.

In two previous studies of Method 8261A, quality control limits were established to ensure that reporting errors were consistent with analytical errors for water [8] and soil [9] and these were used in this study. A critical step to accurately measure contaminants in soil was to ensure that analytes, surrogates, and internal standards were equilibrated with the soil. Attempts to minimize this effect through quick analysis (minimal time for soil and internal standard interactions) can lead to erroneous results [9]. While equilibration of internal standards with sample matrices is not addressed in the method protocols, all analyses used in this study included steps to equilibrate internal standards with the sample matrix, which included mixing internal standards in dry soil. It had been noted that there was a significant difference between Method 8260C/5032 and Method 8261A results when internal standards and analytes were added to soil after dilution with water [9]. This work evaluates the differences when internal standards and analytes are added to dry soil and equilibrated prior to analyses.

All analyses and calibrations were performed prior to implementing quality controls. Therefore, this study provides insight into the costs associated with those controls and if their implementation improves the accuracy of determinations. This work is generally applicable to other pre-concentration methods used with Method 8260C as water-to-air partitioning and boiling point would be major physical properties impacting recovery of volatiles. However, additional properties (not a major consideration during vacuum distillations) such as diffusion or partitioning between a trap phase and vapor phase need to be evaluated.

2. Experimental

2.1. Evaluation Parameters: One point for comparison of Methods 8260C and 8261A use of internal standards was how their different determinations might deviate from known values for an analysis. This deviation was measured as absolute bias to

eliminate cancellation of positive bias with any negative bias results. The magnitude of an average absolute bias for a collection of analytes is an indication how accurate determining an amount of analyte from the collection might be.

Another comparison of the differing internal standard approaches was how well analyses meet quality controls (QC criteria). The quality controls used for this evaluation were the standard deviation of generated calibration curves, comparison of a daily standard to the calibration curve (continuing calibration standard), the response of internal standards in samples to their standard response and the recovery of surrogates. The calibration criteria include both the limit for standard deviation of a calibration curve for an analyte and how much it's continuing calibration standard could deviate from its calibration (20% for Method 8260C and 40% for Method 8261A for both). The limits in how much the response of internal standards in a sample analysis can deviate from its calibration response (relative response) are provided in Table 1. The limits for recoveries of the various surrogate compounds in any sample are also provided in Table 1. When any of the above criteria was not met for an analyte determination the result is classified as not passing quality control (Fail QC).

For the vacuum distillation methods, Method 8261A and Method 5032, it was shown that the primary properties relating to the recovery of compounds were boiling point and relative volatility [11]. In that work a few compounds were used as reference points to relate the ease of vacuum distilling compounds from water to partition coefficients. Because of the importance found for these properties, boiling points and relative volatilities were used to describe the physical differences between an analyte and the corresponding Method 8260C internal standard. Rather than look at each analyte individually, analyte results were grouped relative to how similar they are to their respective 8260C internal standard. Group 1 includes all analytes that have boiling points within 10 °C of their respective ISTD and the natural logarithm of a relative volatility (lnRV) within one of its ISTD. Group 2 includes analytes that have boiling points within 20 °C of its ISTD and lnRV within two of its ISTDs and not in Group 1, Group 3 includes the analytes that have boiling points within 50 °C and within three lnRV of the ISTD and not in Groups 1 or 2, and Group 4 includes the remaining compounds.

2.2. Quantitation: Method 8260C internal standards and surrogates were as recommended in Method 8260C (Table 1). The compound tetrahydrofuran-d_8 was added as a surrogate for the more polar compounds. Reprocessing of the raw data generated for the previous Method 8261A studies [8, 9] was possible as the recommended internal standards for Method 8260C were included in the Method 8261A studies with the exception that 1,2-dichlorobenzene-d_4 was substituted for 1,4-dichlorobenzene-d_4. All raw data used to create Method 8261A calibration curves, continuing calibration and samples were reprocessed as Method 8260C.

The internal standards and surrogates used with Method 8261A are as previously published [9]. The software used to perform calibration and quantitation was SMCReporter 4.2 available from EPA's web pages [10]. Limits for the internal standards and surrogate recoveries as described in the previous studies are presented in Table 1.

2.3. Samples: There were three sources of analyses used in this study. The water analyses had been generated in a previous study [8] investigating the reporting error associated with Method 8261A and these analyses were re-quantified as per Method 8260C/5032. The soil analyses were generated in study [9] reporting error associated with Method 8261A analyses of soil and these analyses were re-quantified as per Method 8260C/5032. The biota results were performed as part of this work and the instrumentation used described in Supplementary Information.

Table 2 lists the matrices studied. Water samples were modified with NaCl (0.1, 0.3, and 1 g), glycerin (0.1, 0.3, and 1 g), detergent (0.05, 0.1 and 0.2 mL), and peanut oil (0.1, and 0.3 g); 5 mL of the modified water samples was analyzed.

Soil samples consisted of acid-washed sand and three top soils, (NV, GA, and OR). As minimal efforts to introduce internal standards were shown to have a potential to understate amounts of VOCs in soil samples [9], only the analyses in that study where the introduction of compounds to soil was rigorous to ensure interaction with the matrix were used. The preparation of soil samples included the additions of internal standards, surrogates, and analytes being added to 5-g dry soil then connected to the distiller (sealed) for overnight equilibration. Five mL water and a magnetic stir bar were added the following day and the mixture stirred with use of a magnetic stirrer prior to distillation.

Biota samples were analyzed for this study to demonstrate severe matrix effects. These samples included 5 g grass, 2.5 g pine needles, 2.5 g rosemary, and 5 g muscle (tuna and shrimp). Fresh (no drying) vegetation samples were ball-milled using a Retsch model MM 301 (Haan, Germany) and transferred to vacuum distiller vessels; 5 mL distilled deionized water was added followed by the internal standards, surrogates and analytes. The vegetation samples were then homogenized using an Omni International GLH homogenizer with 10 mm by 195 mm probe (Marietta, GA) for approximately 1 minute. The tuna and shrimp samples were added to the vacuum distiller vessel, the internal standards, surrogates, and analytes added, then 5 mL distilled deionized water added. The vessel contents were then homogenized for 1-2 minutes.

The amounts of analytes in reagent blanks were negligible compared to the amounts used to fortify the samples. When the amount of an analyte was found present (10% of amount being added) in an unfortified matrix, the analyte was not used for the matrix. If a compound was found to degrade in a matrix (more than 60% in 120 h) it was not considered for the matrix. These considerations made the number of analytes determined for a sample vary by matrix. There were no attempts to further dilute samples in order to mitigate matrix effects. Besides the fact that dilution of sample can make an analysis insensitive, identifying how results were being impacted when a criterion was not met was desired.

3. Results and Discussion

Because of the large number of analytes and determinations, interpretation of results is done as a member of a group (1-4) as described in Sec 2.1. A complete list of analytes and the group they belong is listed in Supplementary Materials.

The initial calibration requirement for any analyte using Method 8260C is that the standard deviation for its response factor is not to exceed 20%. An analyte determination that uses a calibration where this criterion is not met is to be noted as an estimated result. The continuing calibration requirement for a Method 8260C analyte is that when its response factor differs by more than 20% from its initial response factor, then each result for the analyte is reported as an estimate. For Method 8261A a less stringent 40% criterion for both initial calibration and continuing calibration is recommended as a lesser value could not be shown to impact the accuracy of analyte determinations [8]. The more liberal Method 8261A criteria are justified in that the calibration error (standard deviation) is propagated with the Method 8261A calculated analytical error and is reported with each determination.

It was found that as boiling points and lnRV of an analyte group became more dissimilar from their internal standards the more likely members of the group would not meet a calibration criterion. Figure 1 illustrates that the failure rate of an average Method

8260C analyte in Group 1 to be 6% and increased to a 68% failure rate for Group 4. For Method 8261A the failure rates for the same analyte groups were 0 and 15% respectively.

Both Methods 8260C and 8261A analyte determinations had to meet internal standard and surrogate requirements by analyte class (Table 1). Analytes were classified as either, volatile, non-purgeable, or semivolatile as was done for Method 8261A analyses [8]. The volatile class consisted of compounds with a boiling point less than 159 °C and relative volatility less than 100 (lnRV < 4.61), the non-purgeable class was for analytes boiling at less than 159 °C and relative volatility greater than 100, and the semivolatile class with a boiling point greater than 159 °C. If one of the internal standards or surrogates for a class of compounds is outside recovery criteria then the entire class of analyte results is considered as estimated. The internal standard relative response and surrogate recovery limits for Method 8260C analyses were taken from the method and those limits for Method 8261A analyses were previously experimentally determined [8, 9] and all are presented in Table 1.

All determinations of analytes that are members of a group were used to calculate a single average bias for the group (*i.e*., Group 1 analytes for soil matrices in Fig 1). This average bias is calculated as the sum of each bias (absolute value of the % difference that a determination of an analyte varies from the amount of the analyte added to a sample) of every result in a grouping and divided by the number of results. Similar to the increasing failure rate for calibration, the average bias increases from Group 1 to Group 4 for each matrix. Figure 1 illustrates that the magnitude of bias for a Method 8260C determination is closely related to the analyte's dissimilarity to its internal standard.

There were 13 matrices studied and these are listed in Table 2. These matrices were selected to demonstrate a range from simple to complex in order to evaluate matrix effects and were not meant to represent typical samples. Figure 2 shows that as samples become more complex and the amount of organic phase increases (water→soil→biota) the frequency for rejecting results increased for both Method 8260Cand Method 8261A. However, Method 8261A uses a broader range of internal standards to correct recoveries (Table 1), and the resulting recovery corrections account for the greater percentage of acceptable results. The failure rates for Method 8260C internal standards for water, soil and biota matrices were 7.4, 39.8, and 62.5% respectively while for Method 8261A internal standard the failure rates were 2.2, 0, and 5.5%.

Combining all analytes (Group 1-4), the average absolute bias of results that met Method 8260C criteria increased from 10% to over 30% across the range of matrices (Fig 2). This indicates that while implementing the quality controls did drastically reject results, there was no assurance that the results that met criteria would be minimally biased. As a comparison, Method 8261A absolute bias varied between 10% and 20%. For the water samples there was little difference in average bias for both methods however the rate of acceptable results was significantly better for Method 8261A.

Table 3 presents the recovery and bias data for the analyte groupings (Group 1-4) by matrix for Methods 8260C and 8261A. Only results that met quality controls were included as "Pass QC". Results that failed to meet the QC criteria were listed as the "Fail QC" data (*i.e*., they are estimated results). Both the "Pass QC" and "Fail QC" were included in the "All" data. It can be seen that applying the quality controls for Method 8260C analyses generally decreased the average bias of each groups' results for all matrices with greater improvement for groups 2 and 3 analytes. However, applying the quality controls ("Pass QC") did least to lower the bias of Method 8260C determinations for analytes in Groups 1 and 4. Group 1 results were less biased with or without quality controls while group 4 results were more biased with or without the quality controls. These results indicate that group 1 analytes are consistently reliable as they behave closely with their internal standards. Groups 2 and 3 analytes are more reliable after quality controls are implemented. Generally, Group 4 analyte determinations will be more biased regardless of quality

controls. Contrary to these trends seen for Method 8260C determinations, the bias of Method 8261A determinations is less for Groups 2-4 and less impacted by matrix. This is a strong indication that matrix effect is in a large part relative to the physical difference between the analytes and their assigned internal standards.

It is interesting to note that the "Fail QC" (and therefore determinations to be used as qualitative) for Method 8260C Group 1 have a smaller average bias than the "Pass QC" results for Groups 3 and 4. This implies that an estimated determination of a Group 1 analyte is likely more accurate than a Group 3 or 4 analyte determination meeting all quality controls. This demonstrates the need to consider the dissimilarity between an analyte and its internal standard when assessing data quality.

For some of the analyzed matrices most of the Method 8260C generated results that did not pass criteria. In most instances this would likely result in drastically diluting the sample to overcome "matrix effects". A sample diluted to meet quality controls may yield results too insensitive to meet the needs for the analysis while the dilution might have little impact on the bias of analytes in groups 1 and 4.

Method 8260C analytes should have properties similar to their corresponding ISTDs for accurate determinations. The bias for determinations when properties are similar (i.e., boiling points within 10 °C and the natural log of the relative volatility within one) are minimal and the frequency of calibration failure rates low. As analytes become more dissimilar from their ISTDs then the merits of Method 8261A determinations over Method 8260C determination are more pronounced.

The impact of following Method 8260C calibration requirements for a Group 3 or Group 4 analytes to date can only be conjecture. It is hoped that this work will give insight to the source of many calibration problems and prevent unwarranted expectations of minimal calibration errors when analytes differ greatly from their assigned internal standards.

Assessing the impact of a single source of systematic error in the presence of other errors is challenging if not impossible without addressing all major errors in an experimental design. Other errors can be severe when equilibrium between the internal standards and sample has not been established [9]. These were minimized in this study with a thorough mixing and equilibration of internal standards with the matrices. Because "matrix effects" can occur when internal standards interact with a matrix (and cause reanalysis), thorough mixing is not the common practice. Therefore it is unlikely that this work could be used to account for biases seen in other studies. The intent is to better understand a potential major source of bias and when it is necessary to address the selection of Method 8260C internal standards.

Tables of the internal standards, surrogates and analytes are included as supplemental information.

Notice

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Table 1 Summary of acceptable recovery ranges for internal standards and surrogates for Method 8260C and Method 8261A

				Water	Soil
	bp[a]	lnRV[b]	Impacted analyte class[c]	Recovery (%)[d]	Recovery (%)[e]
Internal standards-Method 8260C					
1,4-Difluorobenzene	89	1.34	Volatile, non-purgeable	50 to 200	50 to 200
Chlorobenzene-d_5	131	1.84	Volatile, non-purgeable	50 to 200	50 to 200
1,2-Dichlorobenzene-d_4	181	2.08	Volatile, semivolatile [f]	50 to 200	50 to 200
1,2,4-Trichlorobenzene-d_3	213	2.06	Semivolatile	50 to 200	50 to 200
Surrogates-Method 8260C					
1,2-Dichloroethane-d_4	84	3.00	Volatile	75 to 125	75 to 125
Toluene-d_8	111	1.45	Volatile	75 to 125	75 to 125
4-Bromofluorobenzene	152	1.79	Volatile	75 to 125	75 to 125
Naphthalene-d_8	217	2.89	Semivolatile	75 to 125	75 to 125
Tetrahydrofuran-d_8	66	5.87	Non-purgeable	75 to 125	75 to 125
Internal standards-Method 8261A[g]					
1,4-Difluorobenzene	89	1.34	Volatile, non-purgeable	52 to 156	48 to 141
Chlorobenzene-d_5	131	1.84	Volatile, non-purgeable	45 to 161	27 to 134
1,2-Dichlorobenzene-d_4	181	2.08	Volatile, semivolatile [f]	33 to 168	7 to 136
Tetrahydrofuran-d_8	66	5.87	Non-purgeable	26 to 308	46 to 240
1,4-Dioxane-d_8	101	8.67	Non-purgeable	12 to 941	25 to 176
Naphthalene-d_8	217	2.89	Semivolatile	23 to 252	3 to 191
Surrogates-Method 8261A					
Methylene chloride-d_2	40	2.41	Volatile	68 to 117	62 to 134
Benzene-d_6	79	1.37	Volatile	87 to 109	85 to 115
1,2-Dichloropropane-d_6	96	2.40	Volatile	87 to 108	90 to 110
1,1,2-Trichloroethane-d_3	112	3.28	Volatile	90 to 115	83 to 121
4-Bromofluorobenzene	152	1.79	Volatile	89 to 106	66 to 103
Nitromethane-^{13}C	101	6.23	Non-purgeable	69 to 111	64 to 128
Ethylacetate-^{13}C	77	5.01	Non-purgeable	76 to 125	0 to 124
1,2,4-Trichlorobenzene-d_3	213	2.06	Semivolatile	75 to 125[h]	55 to 103
1-Methylnaphthalene-d_{10}	241	4.20	Semivolatile	75 to 125 [h]	51 to 119

[a] Boiling point of compound

[b] Natural logarithm of compound's relative volatility

[c] Compounds are categorized as volatile, semivolatile or non-purgeable by their physical properties. Volatiles are compounds with boiling points below 159 °C and relative volatility below 100, Semivolatiles have boiling points above 159 °, and non-purgeable have boiling points below 159 °C and relative volatility above 100. The internal standards listed for Method 8260C are selected by retention time and irrespective of relative volatility.

[d] Ranges for Method 8260C are from Method. Ranges for Method 8261A are from reference 7.

[e] Ranges for Method 8260C are from Method. Ranges for Method 8261A are from reference 8.

[f] While the boiling point for the compound belongs to only the semivolatile class it is used as an internal standard for some volatile analytes

[g] The Internal standards used for monitoring relative response as a quality control is a subset of internal standards in method.

[h] Estimated ranges.

Table 2 Sample Matrices

Water	Matrix/modifier	Sample matrix	Organic phase[a] g
	Volumes 5,25 and 50mL	W1	0.
	NaCl	W2	0.
	Glycerin	W3	0.
	Detergent	W4	0.
	Peanut oil	W5	.2
Soils	Sand	S1	0.
	Georgia clay (GA)	S2	.01
	Nevada mountain (NV)	S3	.19
	Oregon farm (OR)	S4	.24
Biota	Grass	B1	1.04
	Pine	B2	1.29
	Rosemary	B3	.66
	Muscle	B4	.92

[a] Organic phase is the total amount in sample. The content in soils is taken from reference 9 and the content in biota was determined as dry weight after 104 °C overnight.

Table 3 Average recovery, standard deviation, and absolute bias of determinations by matrix and group showing impact of quality control

		Group 1[a]				Group 2				Group 3				Group 4			
		avg [b]	dev	Bias[c]	# [d]	avg	dev	bias	#	avg	dev	bias	#	avg	dev	bias	#
Method 8260C																	
Pass QC [f]																	
	Water	102.3	7.7	5.7	1233	103.2	11.2	8.8	2853	102.1	12.5	10.9	2166	94.2	18.4	18.7	573
	Soil	99.5	5.7	7.5	92	104.4	18.0	15.4	240	101.6	22.8	18.9	194	69.5	18.4	34.1	66
	Biota	90.2	5.9	9.8	18	102.2	20.2	18.1	54	86.9	41.8	37.5	39	95.4	41.0	42.0	11
All																	
	Water	102.3	9.7	6.6	1650	104.2	16.6	10.5	3970	103.7	19.5	13.3	3240	92.5	32.7	24.8	2120
	Soil	102.5	13.9	9.5	258	130.7	90.3	35.7	624	118.5	49.7	34.3	474	105.7	48.1	45.7	258
	Biota	102.3	25.4	15.8	242	124.4	81.6	39.8	556	121.2	82.2	50.4	424	101.0	55.1	41.2	282
Fail QC																	
	Water	102.3	14.1	10.2	417	106.8	25.6	16.1	1117	106.9	28.6	19.1	1074	91.9	36.6	29.3	1547
	Soil	104.1	16.6	12.1	166	147.1	111.2	42.1	384	130.2	59.1	40.0	280	118.2	48.8	42.1	192
	Biota	103.2	26.1	14.3	224	126.8	85.3	37.5	502	124.7	84.5	49.7	385	101.2	55.6	35.5	271
Method 8261A																	
Pass QC																	
	Water	100.8	7.7	5.7	1500	103.5	9.3	7.6	3675	102.9	9.1	7.4	3040	95.0	17.3	14.5	1847
	Soil	94.0	12.2	8.8	243	107.3	22.2	10.6	573	99.5	15.8	11.2	429	100.2	20.0	16.8	243
	Biota	93.9	11.4	10.5	22	98.7	10.2	7.8	72	99.8	15.3	9.4	64	108.0	27.9	20.2	119
All																	
	Water	100.0	9.1	6.4	1650	103.1	10.0	8.0	3970	102.1	11.0	8.1	3240	93.5	20.3	16.1	2120
	Soil	94.3	12.1	8.9	258	107.0	21.5	10.7	624	98.2	16.2	11.5	474	99.0	20.8	17.1	258
	Biota	89.4	19.2	16.1	242	98.0	25.7	16.6	556	92.5	31.5	20.6	424	99.6	29.3	22.0	282
Fail QC																	
	Water	92.1	15.6	11.0	150	97.3	15.8	11.9	295	91.0	23.8	12.9	200	83.3	32.8	23.6	273
	Soil	98.5	8.8	5.8	15	103.8	11.8	8.8	51	95.0	18.8	14.5	45	79.5	24.9	25.0	15
	Biota	88.9	19.8	16.1	220	97.9	27.2	16.8	484	91.3	33.4	22.9	360	93.4	28.9	23.4	163

[a] Group 1contains compounds that have boiling points and lnRV within 10 °C and 1 of their internal standards, Group 2 are those within 20 °C and 2, Group 3 50 °C and 3 and Group 4 contains the remaining compounds. Method 8261A results are for the same analytes for comparison. Columns are for average recovery and standard deviation,

[b] Average and standard deviation of each result in category.

[c] Bias is calculated as the sum of each bias (absolute value of the % difference that a determination of an analyte varies from the amount of the analyte added to a sample) of every result in a grouping and divided by the number of results.

[d] Number of determinations.

[f] Results are listed by method and if quality controls have been implemented. "Pass-QC" includes only results that meet criteria, "Fail QC" include only those results that failed to meet criteria, and "All" includes both "Pass QC" and "Fail QC."

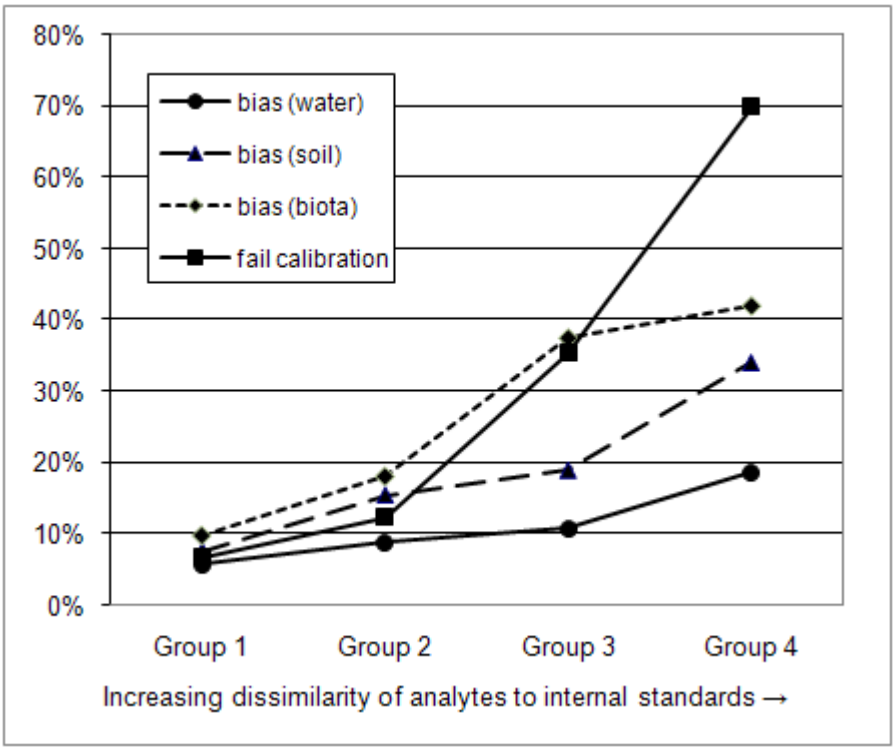

Figure 1. Bias and a failure to meet calibration criteria compared to dissimilarity between analyte and internal standards.

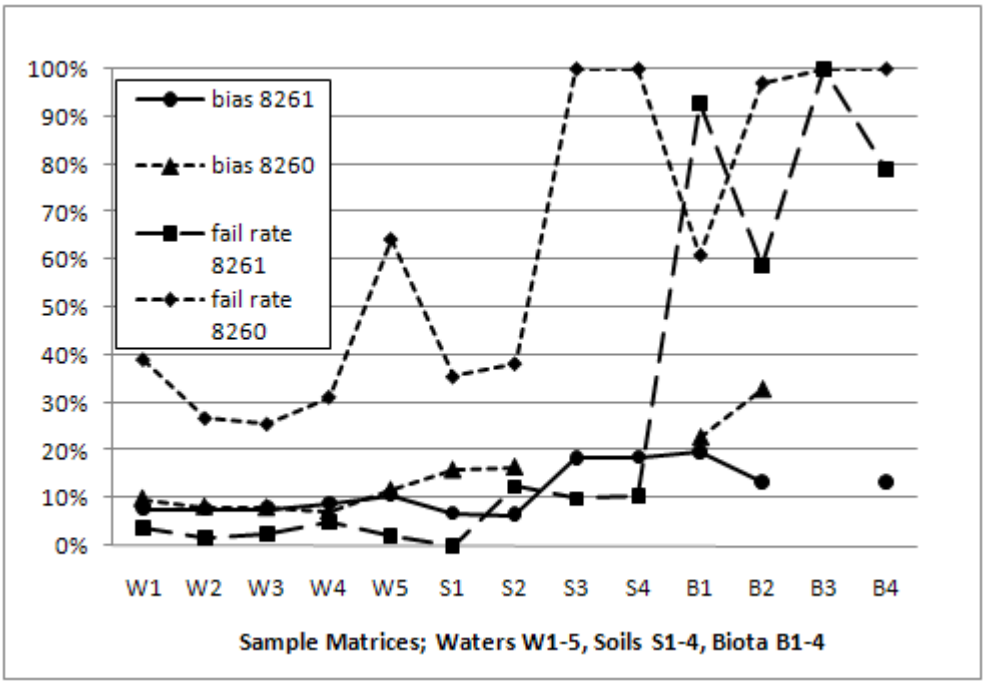

Figure 2. Determination bias (absolute) and frequency of failing quality controls for Methods 8260C and 8261A by matrix.