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...H-PERFORMANCE, LIQUID-CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN WATER

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Several natural water samples were fortified with mixtures of polynuclear aromatic hydrocarbons containing naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, chrysene, 1,2-benzanthracene, benzo(a)pyrene, 1,2:5,6-dibenzanthracene, and benzo(g,h,i)perylene. Resulting solutions, with concentrations of individual polynuclear aromatic hydrocarbons ranging from 0.05 to 11.0 micrograms per liter, were analyzed by high-performance liquid chromatography to investigate limits of method applicability and to acquire necessary precision data.

The polynuclear aromatic hydrocarbons considered in this study were detected in the micrograms per liter range and were found to have a total chromatographic elution time of approximately 35 minutes. Successive determinations of standard mixtures, followed by statistical analysis of the data, showed an average mean recovery of 83.1 percent, an average standard deviation of ±0.130 microgram per liter, and an average relative standard deviation of 7.45 percent.

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ABSTRACT

High-performance liquid chromatography provides a rapid and sensitive means for determining polynuclear aromatic hydrocarbons in water samples. A high-performance liquid chromatograph, coupled with ultraviolet or fluorescence detectors has greater selectivity for analysis than methods using gas-chromatographic and flame-ionization systems.

Several natural water samples were fortified with mixtures of polynuclear aromatic hydrocarbons containing naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, chrysene, 1,2-benzanthracene, benzo(a)pyrene, 1,2:5,6-dibenzanthracene, and benzo(g,h,i)perylene. Resulting solutions, with concentrations of individual polynuclear aromatic hydrocarbons ranging from 0.05 to 11.0 micrograms per liter, were analyzed by high-performance liquid chromatography to investigate limits of method applicability and to acquire necessary precision data.

The polynuclear aromatic hydrocarbons considered in this study were detected in the micrograms per liter range and were found to have a total chromatographic elution time of approximately 35 minutes. Successive determinations of standard mixtures, followed by statistical analysis of the data, showed an average mean recovery of 83.1 percent, an average standard deviation of ± 0.130 microgram per liter, and an average relative standard deviation of 7.45 percent.

INTRODUCTION

Several polynuclear aromatic hydrocarbons (PNA's) are known to be potent mutagens (Josephson, 1981) and carcinogens (Badger, 1962; Hueper and Conway, 1964; World Health Organization, 1971); this fact has caused this chemical class to be studied extensively. The presence of PNA's in such media as industrial- and municipal-waste effluents, surface and ground waters, and associated sediments, necessitates the development of analytical procedures for these ubiquitous substances that are introduced into water systems via rain runoff from asphalt highways, rainfall through polluted air, or directly from industrial-plant discharge. Natural sources for PNA's may be from endogenous formation in plants. Because the water solubility of PNA's is minimal, their adsorption onto colloidal material, bacterial growth, and suspended sediment serves as a transportation mechanism in water (Harrison and others, 1976). Although sediments have been extracted and analyzed for PNA's (Giger and Schaffner, 1978; Lee and Wright, 1980) by glass-capillary gas chromatography, this report focuses on the analysis of PNA's in water by high-performance liquid chromatography.

A priority pollutant list was compiled by the U.S. Environmental Protection Agency in response to a congressional request. This list, as reported by Keith and Telliard (1979) includes 16 PNA's. During the initial stages of this study, only 12 PNA's were available to use as standards for this method.

Certain characteristic properties of PNA's contribute to minimal recovery; therefore, time between onsite sampling and laboratory analysis needs to be as short as possible. PNA's are known to be sensitive to the light (Kuratsune and Hirohata, 1962); to undergo possible rearrangement (Krstulovic and others, 1977); and to adhere to the walls of glass containers (Acheson and others, 1976). Harrison and others (1976) noted that time delays, coupled with stirring, contributed to significant PNA losses. Junk and others (1974) studied the effect of the shape of the concentration vessel on PNA recovery; they recommend the use of a Kuderna-Danish concentration apparatus that was used in developing the method described in this report. Moreover, the addition of the acetonitrile minimized losses during concentration of the extracts.

Some industrial-effluent and wastewater extracts may require a clean-up procedure prior to analysis. Because most water samples analyzed in the U.S. Geological Survey laboratories originate from relatively clean surface and ground waters, adsorption clean-up was not required and was not investigated.

Ultraviolet and fluorescence detectors have been recommended as the detectors for analysis of PNA's using high-performance liquid chromatography (Harrison and others, 1975). The ultraviolet detector was selected for this method. A particular PNA can be identified by determining the ratio of the absorbance at a wavelength of 254 nm (nanometers) to the absorbance at a wavelength of 313 nm in a standard solution. This ratio

was used to identify certain PNA's, described in subsequent paragraphs. At certain excitation and emission wavelengths, fluorescence detection allows greater sensitivity for certain PNA's. The fluorescence detector could be used in series with the ultraviolet detector to yield additional confirmatory information; however, a fluorescence detector was not used in developing this method. This method was developed with commercially available equipment to obtain the desired precision and accuracy.

METHOD

1. Summary of Method

Samples were collected in clean glass bottles that were heated at 300°C (degrees Celsius) overnight, and were fitted with Teflon[1]-lined lids. Samples were shipped to the laboratory and maintained under refrigeration at 4°C, until extracted. Each sample was weighed and extracted with methylene chloride. Each extract was dried over sodium sulfate and concentrated in two stages: (1) in a Kuderna-Danish apparatus; and (2) in an analytical-evaporative concentrator (Goerlitz and Brown, 1972). A few microliters of the sample extract were injected into the high-performance liquid chromatograph. Qualitative and quantitative analyses were conducted using an external standard, and final concentrations were reported in micrograms per liter.

2. Application

This method is suitable for determination of PNA's in natural waters. If a large amount of sediment is present, the sample needs to be filtered and the filtrate extracted and analyzed according to this method; this will probably give smaller concentrations compared to a whole-water analysis, because PNA's are adsorbed onto sediment particles. Concentrations in the micrograms per liter range can be detected for each of the 12 PNA's, using an ultraviolet detector, because they have large extinction coefficients. The 12 PNA's analyzed by this method were naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, benzo(a)anthracene, chrysene, benzo(a)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.

3. Interference

3.1 Interferences may result from compounds found in natural waters that have absorbance at analytical wavelengths. Depending on sample source and matrix, a column adsorption clean-up may be necessary. Natural surface waters from several States in the Western United States were used as spiking media. Additional clean-up was not necessary.

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[1]Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

3.2 A blank was included with each group of samples to ascertain purity of solvents, reagents, and equipment.

3.3 Filtration of both organic and aqueous analytical solvents was required to degas and to remove particulates from solvents. After the system had equilibrated, a blank-gradient run with no injection was performed to determine the presence of interferences in the dual-solvent mixture and in the instrument.

3.4 Suspended sediment, if present in concentrations greater than 100 milligrams per liter, needs to be removed by filtration, and resultant filtrate used for analysis.

4. Apparatus

All glassware was washed in a warm-detergent solution, rinsed with organic-free water and heated at 350°C overnight. All glassware was rinsed with solvent immediately before use.

4.1 Balance: Cahn model 4100 electrobalance or equivalent.

4.2 Balance: single pan, Mettler PN2210 or equivalent.

4.3 Concentrator: the Meyer N-Evap evaporative concentrator or equivalent. Extracts were concentrated using a gentle flow of inert gas (usually dry nitrogen).

4.4 Extractor: 1,000-mL (milliliter) separatory funnel with a Teflon stopcock, ringstand, and a 125-mL Erlenmeyer flask for extract collection.

4.5 Filtering apparatus: Millipore, 250-mL reservoir with a glass frit, and a 1,000-mL receiving reservoir with HF and HA 0.45-µm (micrometer) filters for the corresponding organic and aqueous solvents, or equivalent.

4.6 High-performance liquid chromatographic system: including a liquid chromatograph capable of a linear-solvent, gradient-elution program, a dual-channel ultraviolet detector, a reverse-phase C_{18}-(10 µm) column, a 10-mV (millivolt) recorder and a 25-µL (microliter) syringe, or equivalent. A Waters Associates Model ALC/GPC-244 liquid chromatograph was used with a Model 6000A solvent delivery system, a Waters Associates micro-Bondapak C_{18}-reverse-phase column (part no. 27324), a model U6K injector, a Hamilton 802RN syringe with U6K needle adaptor, a dual-channel Waters Associates Model 440 ultraviolet-absorbance detector, and a Houston Omni-Scribe dual-pen recorder.

4.7 Kuderna-Danish Concentrator: consists of three all-glass sections: (1) The top section is a three-ball Snyder column; (2) the middle section is a 250-mL concentrator body; and (3) the bottom section is either a 10-mL or a 4-mL capacity receiver.

4.8 Steam bath: temperature equilibrated to 75-85°C, fitted with concentric rings to hold the Kuderna-Danish apparatus.

4.9 Volumetric flasks: 25-mL capacity, used to prepare the stock and working-standard solutions.

5. Reagents

5.1 Acetonitrile: high-performance, liquid-chromatographic grade.

5.2 Methylene chloride: high-performance, liquid-chromatographic grade.

5.3 PNA stock solutions: 12 PNA's were weighed on the electrobalance and transferred to a volumetric flask. Methylene chloride was used as a solvent to provide stock solutions in the approximate 100-300 ng/μL (nanograms per microliter) concentration range. Purity certified, PNA standards were obtained from commercial chemical-specialty suppliers and the Quality Assurance Section of the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. The following PNA's were used to prepare stocks that were stored in the dark at 4°C: (1) Napthalene, (2) acenaphthene, (3) fluorene, (4) phenanthrene, (5) anthracene, (6) pyrene, (7) fluoranthene, (8) benzo(a)anthracene, (9) chrysene, (10) benzo(a)pyrene, (11) dibenzo(a,h)anthracene, (12) benzo(g,h,i)perylene.

5.4 PNA working-standard solution: a mixture of 12 polynuclear aromatic hydrocarbons in the low ng/μL concentration range. This standard was prepared by diluting individual stock solutions with acetonitrile.

5.5 Sodium sulfate: anhydrous, granular, and heated overnight at 300°C.

5.6 Water: high-performance, liquid chromatographic grade or equivalent containing no ultraviolet absorbing compounds as determined by a blank-gradient analysis; deionized water treated with a Millipore multicartridge purification system was acceptable.

6. Procedure

6.1 Calibration: the chromatographic system was calibrated prior to sample determinations by analyzing 4-5 μL of a PNA working standard. The volume injected was measured and each PNA response factor calculated to determine retention times of the 12 PNA's and to serve as an overall-system check. The retention time is from the time the sample was injected to the time the appropriate PNA appeared on the chromatogram at its maximum height. The response factor, expressed in nanograms per count, was calculated from the number of microliters of the standard PNA injected, multiplied by the concentration (nanograms per microliter) of that PNA in the standard, and divided by the integrator area counts produced by that particular PNA (see 7.2.1).

The concentration of each PNA in the working-standard mixture is listed in table 1. Napthalene was the earliest eluting PNA. At the 254-nm wavelength, the K' or capacity factor for napthalene was 3.61. The capacity factor, K', is defined as the retention of a compound in terms of solvent volumes; the non-retained peak or column void volume (V_o) is subtracted from the component retention volume (V_1), and the result is divided by the column void volume (V_o):

$$\text{Capacity factor} \qquad (K') = \frac{V_1 - V_o}{V_o} .$$

Capacity factors ranged from 3.61 for napthalene to 7.60 for benzo(g,h,i,)perylene.

6.2 Sampling: Goerlitz and Brown (1972) describe a sampling procedure for water samples that require organic analyses. The sample bottles were washed with detergent, rinsed thoroughly with tap water, and rinsed with organic-free distilled water. The glass bottles were heated overnight at 350°C to oxidize any residual organic material. Teflon-lined caps were used. After collection, the sample was cooled with ice or refrigerated at 4°C. The sample was packed to avoid possible breakage during transportation and shipped to the laboratory without delay. No preservatives were added. Samples were extracted immediately upon receipt in the laboratory.

6.3 Extraction: weigh the approximate 1-liter sample bottle and lid and record the weight.

Table 1.--*Concentrations of polynuclear aromatic hydrocarbons in working-standard mixture*

Polynuclear aromatic hydrocarbon	Concentration (nanograms per microliter)
napthalene	5.14
acenaphthene	10.8
fluorene	2.57
phenanthrene	.82
anthracene	.21
pyrene	1.28
fluoranthene	5.54
benzo(a)anthracene	1.70
chrysene	2.56
benzo(a)pyrene	.58
dibenzo(a,h)anthracene	.51
benzo(g,h,i)perylene	6.40

6.3.1 Set up the extraction apparatus, consisting of separatory funnels, rings, and ringstands. Pour the sample into the separatory funnel and add 40 mL of methylene chloride. Shake the funnel for at least 1 minute, venting frequently. Allow the layers to separate. Withdraw the lower methylene-chloride layer into a 125-mL Erlenmeyer flask. Repeat for a total of three extractions and combine all extracts.

6.3.2 Weigh the empty sample bottle and cap. Subtract this weight from the original weight to determine the volume of the water sample that was extracted [1.00 g (gram) = 1.00 mL at 4°C].

6.3.3 Add approximately 0.5 g of sodium sulfate to the extract, cover, and store in the refrigerator for at least 2 hours.

6.3.4 Attach the Kuderna-Danish apparatus to a receiver and quantitatively transfer the organic extract to the concentration vessel. Add a small boiling chip and 0.5 mL of acetonitrile; connect the three-ball Snyder column; and place the Kuderna-Danish apparatus on the steam bath. Remove the Kuderna-Danish apparatus immediately before the glass balls stop bouncing and allow the apparatus to cool.

6.3.5 Dismantle the Kuderna-Danish apparatus, and place the receiver on the evaporative concentrator. Concentrate the extract to less than 0.5 mL but not to dryness. Dilute with acetonitrile. CAUTION: Steps 6.3.3 and 6.3.4 are critical and need to be conducted carefully to avoid losses of PNA's.

6.3.6 Stopper the receiver and store the sample extract in an explosion-proof refrigerator at 4°C; the extract is ready for analysis and needs to be analyzed as soon as possible.

6.4 Analysis: after filtering and degassing the organic and aqueous solvents, start the analyzer. Allow the system to equilibrate.

6.4.1 Inject about 5 µL of a PNA working standard to determine retention times and response factors (as described in section 6.1). Refer to table 2 for the operating parameters.

6.4.2 Inject 1 µL portion of the sample extract onto the column; be sure no particulate matter was introduced. The column is a reverse-phase, 10-µ, C_{18}-column with a guard column packed with C_{18}-packing (replaced weekly), and a column pre-filter consisting of a 2-µ stainless-steel filter. Working standards need to be injected at the beginning, the end, and at the interval of every four samples in the set to be analyzed.

6.4.3 Qualitative analysis was performed by comparing retention times of the working standard with those found in the extract (see calibration, 6.1). The use of absorbance ratioing of two wavelengths (254 and 313 nm) provided qualitative identification, because the peak-area ratio

for a specific PNA is constant. The ultraviolet detector set at the wavelengths of 254 and 313 nm was used to detect all 12 PNA's in a single analysis.

Table 2.--*Results of high-performance liquid chromatography of polynuclear aromatic hydrocarbons*

Compound[1]	Retention time (minutes)	Capacity factor (K')
naphthalene	18.2	3.61
acenaphthene	22.0	4.56
fluorene	22.2	4.65
phenanthrene	23.0	4.83
anthracene	23.7	4.98
fluoranthrene	25.2	5.39
pyrene	25.9	5.48
chrysene	28.1	6.12
1,2-benzanthracene	28.8	6.26
benzo(a)pyrene	31.0	6.85
1,2:5,6-dibenzanthracene	32.9	7.35
benzo(g,h,i)perylene	33.9	7.60

[1] Instrument: Waters Associates Model 440 ultraviolet-absorbance detector at 254 and 313 nanometers; attenuation = 0.01.
Column: Reverse-phase, micro-Bondapak C_{18} - 10-μ (Waters Associates part no. 27324).
Conditions: 40-80 percent CH_3CN/H_2O; linear slope gradient; chartspeed = 1.0 centimeter per minute; run time = 25 minutes; and flow rate = 1.0 milliliter per minute.
Sample: 4 microliters of PNA spiking solution in acetone (see section 9).

6.4.4 The 254-nm detector did not resolve some pairs of compounds; therefore, another wavelength, 313 nm, was needed to distinguish between these pairs. For example, fluorene and acenaphthene each absorb at 254 nm and were not separated by the column. Acenaphthene however, absorbs at 313 nm; fluorene does not. The response ratio of acenaphthene calculated at 254 nm and 313 nm is 1:1; therefore, both peaks were analyzed. Chrysene and benzo(a)anthracene were not clearly distinguishable at 254 nm, but are at 313 nm. Thus, when these compounds were analyzed at both wavelengths, individual contributions to peak areas were determined.

7. Calculations

The liquid-chromatographic system was calibrated with two standard-working solutions at different concentrations. Electronic integration

was used to determine peak areas in analog to digital counts. Response factors were calculated and reported as nanograms per count (unit) of compound.

7.1 Qualitative analysis: the identification of a PNA in a sample extract was achieved when sample and standard retention times matched. Because the ratio between the 254-nm response and the 313-nm response for a certain PNA is constant, it also was used for identification.

7.2 Quantitative analysis: the chromatographic-peak area was measured by electronic integration.

7.2.1 Sample calculation: the final concentration of the PNA was determined according to the equation:

$$C = \frac{(A)(B)(D)(E)}{(F)(G)}$$

where:

C = final concentration, in micrograms per liter;
A = the response factor (see procedure 6.1), in nanograms per unit;
B = sample area units;
D = dilution factor;
E = final volume of the extract, in microliters;
F = volume of sample injected, in microliters; and
G = volume of the sample, in milliliters.

8. Reporting results

8.1 Report individual PNA's as follows: Less than 10 µg/L, one significant figure; 10 µg/L and greater, two significant figures.

9. Precision and accuracy

Precision and accuracy of this method were determined by spiking three sets of natural-water samples with a PNA spiking solution. The PNA spiking solution was prepared from PNA stock solutions similar to the PNA working solution, except the diluting solvent was acetone, not acetonitrile. A set consisted of seven samples and a blank sample. The water samples were spiked at three levels in the microgram per liter concentration range. Standard deviation ranged from ±0.002 to ±1.17 µg/L, and average standard deviation throughout this spiking range was ±0.130 µg/L. The percentage of mean recovery ranged from 47.6 to 108 percent, with an average mean recovery of 83.1 percent. Relative standard deviation ranged from 2.77 to 24.2 percent, resulting in an average of 7.45 percent. The total error (expressed in percent) (McFarren and others, 1970) ranged from 11.3 to 75.4 percent for an average total error of 28.8 percent.

DISCUSSION OF RESULTS

Using the format set forth in Analytical Chemistry (1979), table 3 summarizes the mean, standard deviation, percentage of mean recovery, percentage of relative standard deviation, and percentage of total error (McFarren and others, 1970) found in the analytical method. Three concentration levels, low (L), medium (M), and high (H) were determined on 12 PNA's. Overall average mean recovery of 83.1 percent and average total error of 28.8 percent are within acceptable limits for method approval. Earlier eluting PNA's have a smaller percentage of recovery, because their vapor pressure is greater; therefore, their losses are greater during concentration steps.

Naphthalene had the smallest percentage of recovery, due to concentration and photochemical losses. Kuratsune and Hirohata (1962) reported that naphthalene was the most light-sensitive of the PNA's; 47 percent decomposed during 41 hours of fluorescent illumination.

The original recovery work outlined in table 3 was performed using the Waters Associates 10-μ C_{18} micro-Bondapak column. Beckman Instruments 5-μ C_{18}-Ultrasphere column was evaluated at a later date. This column provided better resolution, but required slightly longer analysis time. If an autosampler were used, this longer analysis time would not be a disadvantage, and the significant increase in resolution would favor use of the Ultrasphere column. For example, the 10-μ column gave 6,500 theoretical plates, while the 5-μ column gave 36,000 theoretical plates for naphthalene.

Table 3.--*Recovery of polynuclear aromatic hydrocarbons from native-water samples*

[PNA = polynuclear aromatic hydrocarbon; µg/L = micrograms per liter;
Concentration levels: L, Low; M, Medium; H, High;
(1) through (12) are PNA numbers; (1) through (7) are sample numbers]

PNA No.	(1)	(2)	(3)	(4)	(5)	(6)
	Naphthalene	Fluorene	Acenaphthene	Phenanthracene	Anthracene	Pyrene
PNA amount spiked (µg/L)	1.28	0.64	2.75	0.21	0.052	0.32
L-1	0.87	0.41	1.84	0.15	0.037	0.29
L-2	.96	.47	2.01	.16	.037	.28
L-3	.87	.41	1.84	.15	.037	.29
L-4	.95	.47	1.84	.13	.037	.29
L-5	.93	.48	2.17	.15	.037	.29
L-6	.96	.52	2.17	.16	.040	.27
L-7	1.06	.56	2.20	.17	.040	.28
Mean	0.94	0.47	2.01	0.15	0.038	0.28
Standard deviation	.065	.054	0.170	.013	.0015	.0079
Percentage of mean recovery	73.7	74.1	73.1	72.8	72.8	88.8
Percentage of relative standard deviation	6.86	11.5	8.46	8.33	3.86	2.77
Percentage of total error	36.4	42.9	39.3	39.1	32.8	16.1
PNA amount added (µg/L)	2.56	1.28	5.50	0.42	0.104	0.64
M-1	1.10	0.81	3.52	0.33	0.070	0.56
M-2	1.56	1.01	4.02	.36	.079	.56
M-3	1.82	.99	4.02	.36	.078	.58
M-4	1.74	1.01	4.02	.39	.079	.58
M-5	1.23	.90	3.02	.37	.075	.58
M-6	1.33	.93	3.52	.39	.081	.62
M-7	1.18	.90	3.02	.34	.073	.58
Mean	1.42	0.94	3.59	0.36	0.076	0.58
Standard deviation	.285	.073	.45	.023	.004	.02
Percentage of mean recovery	55.6	73.1	65.3	86.4	73.5	90.6
Percentage of relative standard deviation	20.0	7.84	12.5	6.30	5.12	3.43
Percentage of total error	66.7	38.4	51.1	24.5	34.0	15.6
PNA amount added (µg/L)	5.12	2.56	11.0	0.84	0.208	1.28
H-1	2.30	1.41	5.06	0.64	0.135	1.08
H-2	2.20	1.51	6.27	.64	.137	1.18
H-3	3.43	1.89	8.58	.73	.158	1.22
H-4	1.74	1.43	5.50	.62	.131	1.04
H-5	2.36	1.64	6.27	.67	.139	1.15
H-6	3.02	2.02	7.37	.75	.156	1.18
H-7	2.00	1.54	6.38	.60	.141	1.10
Mean	2.44	1.63	6.49	0.66	0.142	1.14
Standard deviation	.589	.235	1.17	.056	.010	.064
Percentage of mean recovery	47.6	63.8	59.0	79.1	68.5	88.7
Percentage of relative standard deviation	24.2	14.4	18.0	8.46	7.43	5.63
Percentage of total error	75.4	54.5	62.3	34.3	41.6	21.3

Table 3.--*Recovery of polynuclear aromatic hydrocarbons from native-water samples*--Continued

PNA No.	(7) Fluoranthene	(8) Benzo(a) anthracene	(9) Chrysene	(10) Benzo(a) pyrene	(11) Dibenzo(a,h) anthracene	(12) Benzo(g,h,i) perylene
PNA amount spiked (µg/L)	1.38	0.425	0.64	0.145	0.128	0.160
L-1	1.10	0.391	0.57	0.126	0.111	1.39
L-2	1.14	.391	.57	.126	.116	1.41
L-3	1.10	.391	.57	.126	.111	1.39
L-4	1.10	.374	.53	.120	.111	1.33
L-5	1.21	.408	.61	.138	.128	1.46
L-6	1.14	.408	.54	.135	.128	1.39
L-7	1.17	.391	.60	.126	.111	1.44
Mean	1.13	0.393	0.57	0.128	0.117	1.40
Standard deviation	0.039	.012	.029	.0062	.008	.042
Percentage of mean recovery	82.1	92.6	89.1	88.4	91.1	87.6
Percentage of relative standard deviation	3.49	2.98	5.07	4.82	6.88	2.98
Percentage of total error	23.6	12.9	19.9	20.1	21.4	17.6
PNA amount added (µg/L)	2.76	0.85	1.28	0.29	0.256	3.2
M-1	2.26	0.77	1.28	0.26	0.256	2.91
M-2	2.35	.81	1.28	.28	.271	3.17
M-3	2.43	.81	1.19	.27	.241	3.07
M-4	2.51	.81	1.28	.30	.287	3.33
M-5	2.51	.77	1.37	.29	.287	3.20
M-6	2.68	.85	1.37	.32	.302	3.49
M-7	2.51	.81	1.37	.31	.287	3.26
Mean	2.46	0.80	1.31	0.29	0.276	3.20
Standard deviation	.135	.028	.068	.022	.020	.185
Percentage of mean recovery	89.3	94.6	102.	100.	108.	100.
Percentage of relative standard deviation	5.46	3.43	5.19	7.45	7.39	5.79
Percentage of total error	20.5	11.9	12.6	14.9	23.8	11.7
PNA amount added (µg/L)	5.52	1.70	2.56	0.58	0.512	6.4
H-1	4.80	1.50	2.41	0.54	0.512	6.21
H-2	4.97	1.70	2.43	.57	.492	6.08
H-3	5.24	1.56	2.18	.59	.532	6.4
H-4	4.64	1.50	2.30	.53	.466	5.82
H-5	4.86	1.63	2.43	.57	.492	6.27
H-6	5.35	1.70	2.56	.55	.486	6.46
H-7	4.86	1.53	2.07	.50	.461	5.89
Mean	4.96	1.59	2.34	0.55	0.492	6.16
Standard deviation	.251	.088	.168	.03	.025	.24
Percentage of mean recovery	89.9	93.4	91.4	94.8	96.0	96.3
Percentage of relative standard deviation	5.06	5.54	7.18	5.45	5.02	3.96
Percentage of total error	19.2	16.9	21.7	15.5	13.6	11.3

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