Analysis of PAHs in Ambient Air, Soil and Emission Samples by GC-MS Isotope Dilution Recovery-corrected Technique

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Introduction:
Environment Canada has been monitoring PAHs as well as other air pollutants since the early '80s through a joint federal-provincial program, the National Air Pollution Surveillance Program [1,2] . The first analytical measurements of PAHs in the early '80s were carried out using packed column gas chromatography with flame ionization detection. By the mid-'80s PAHs analysis was performed using more sensitive and selective techniques (i.e., GC-MS) using capillary column and quadrupole mass selective detector. Improvements over the last ten years in column phase and bonding as well as in the sensitivity of the quadrupole mass spectrometer have led to better separation and lower detection levels of the target compounds.

Recent progress in our analytical methodology involves using the isotope dilution technique to quantify PAHs and account for analyte loss inherent to the analytical process. A sample is spiked with a known amount of isotopically-labelled analytes, referred to as surrogates. The relative response factor of the surrogate to the corresponding native analyte is used to quantify analyte concentration in samples. The principal assumption in isotope dilution is that the chemical and physical properties between the analyte and the isotopic (deuterated or ^{13}C-labelled) analogue are almost identical. Providing that the sample is homogeneous and that the isotopic equilibrium has been reached the recovery of native analyte and its isotopically-labelled analogue from the analytical process should be identical [3] . For the purposes of our method 17 surrogates were chosen to represent 30 native analytes. An average relative response factor using surrogates which are closest in chemical properties to the native analyte is used for natives with no corresponding isotopic analogue.

Quantitation with isotope dilution recovery-correction technique does not require total recovery of analyte since it compensates for matrix effects, analytical process loss and analyte transformations. Monitoring of surrogate recoveries for quality control purposes ensures accurate and reliable recovery-corrected quantitation of the analytes. The acceptable range of surrogate recoveries in the method is 50 to 120 %, with no more than two surrogates outside of these limits.

Use of isotope dilution corrects native analyte concentration for negative bias. This technique has been applied to the quantitation of PAHs in various environmental matrices. The results indicate unambiguously that the isotope dilution technique provides a truer reflection of PAHs levels as indicated by the more consistent distribution of PAHs observed in the recovery-corrected data. A significant difference between the non-recovery corrected and the recovery-corrected results is observed for samples with low recoveries.

PAHs results from 2003/2004 control samples are presented. Future work will involve presenting the validation results and the results of a comparative study of PAHs in ambient air, soil and diesel emission samples, with and without isotope dilution.

Materials and Methods:
NIST Standard Reference Materials were used as controls for PAHs determination in diesel emissions (SRM 2975, SRM 1650a, SRM 1650) and ambient air (SRM 1649a). Soil samples were analyzed as part of the Canadian Association of Environmental Analytical Laboratories (CAEAL) Proficiency Testing Program. The deuterated surrogates used for recovery correction and as internal standards (d_8-Naphthalene, d_8-Acenaphthylene, d_{10}-Acenaphthene, d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Anthracene, d_{10}-Pyrene, d_{12}-Benzo(a)anthracene, d_{12}-Triphenylene, d_{12}-Chrysene, d_{12}-Benzo(b)fluoranthene, d_{12}-Benzo(e)pyrene, d_{12}-Benzo(a)pyrene, d_{12}-Perylene, d_{12}-Indeno(1,2,3-cd)pyrene, d_{14}-Dibenzo(a,h)anthracene, d_{12}-Benzo(g,h,i)perylene, and d_{10}-Fluoranthene as internal standard), with 99 % purity or greater, were obtained from CDN Isotopes, Pointe-Claire, QC, Canada. Sample preparation and analysis were performed using Environment Canada-AAQD methods: 3.3/4.2/M Analytical Method

for the Determination of PAHs in Ambient Air and Diesel Emission Samples, and 3.8/2.3/M Analytical Method for the Determination of PAHs in Soils/Sediments. Analytical analysis was performed with an Agilent 6890 GC interfaced directly to an Agilent 5973 Mass Selective Detector. A 1 µL cool on-column injection was made with an Agilent 7683 Autosampler. A DB-XLB capillary column (30 m x 0.25 mm ID, 0.25 µm film thickness) from J&W Scientific Inc. was used for the separation of PAHs. Analysis was performed using electron impact ionization and selected ion monitoring. A minimum of three ions were monitored for all native analytes, two characteristic ions for each of the surrogate analytes and one ion for the internal standard. The target PAHs were quantified using both isotope dilution and non-recovery corrected procedures. Surrogate recoveries were estimated against an internal standard method. Enhanced Data Analysis MSD ChemStation Software, version D.01.00, was used for data processing. Statistical data treatment was performed with ANOVA analysis using the Microsoft Excel 2003 SP3. Outliers, standard deviation, mean, and significance test with confidence limits of 95% were estimated based on the methods of Miller and Miller [4] .

Results and Discussion:

Non-recovery corrected quantitation: Evaluation of surrogate recoveries spiked in control samples confirmed that the values were within the acceptable range of 50 – 120 % (Figure 1.1). The non-recovery corrected data shows that the ambient air samples have lowest negative bias due to the relatively inert matrix of the ambient air. Soil and diesel matrices had 10 % higher negative bias.

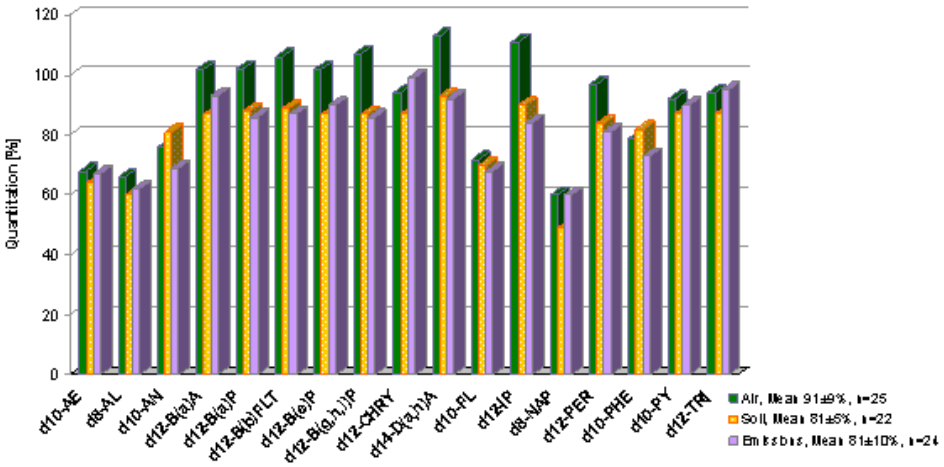

Figure 1.1: PAHs Surrogate Recoveries from Environmental Samples in 2003-2004

ANOVA analysis of the quantitation results was used to demonstrate similarity between native and corresponding surrogate recoveries. The test comparing two experimental means (native and surrogate recoveries) for each matrix confirmed strong similarity between native and surrogate results and no evidence of systematic error at P=0.05. Consequently, it confirms the similar behaviour of isotopes and natives in the analytical process and the reasoning behind using isotopically-labelled analytes as surrogates.

Figure 1.2: Method Bias in Environmental Control Samples corrected and non-corrected

Recovery-corrected (isotope dilution) quantitation: Figure 1.2 shows a decrease in negative bias attributed to analyte loss during the analytical process for the three environmental matrices. The recovery-corrected quantitation of PAHs in ambient air and diesel emission control samples were within 15% of the expected value (88 ± 15 % and 87 ± 11 % respectively). Non-recovery corrected quantitation of PAHs provided lower values (85 ± 16 for air and 79 ± 11 % for diesel emission). Diesel emission samples have lower recoveries therefore greater negative bias. Recovery correction reduces the bias to a value similar to that of ambient air.

Recovery-corrected (isotope dilution) quantitation of PAHs in soil shows higher native concentrations compared to non-corrected data. However, in this matrix, the difference between the two means (recovery-corrected and non-corrected) is much more pronounced than in air or diesel. It is assumed that certain natives have high analytical losses and their corresponding surrogates will also have high losses. Recovery corrected native concentration reflects more accurately the true value. For samples with low recoveries it is expected that there will be a significant difference between the non-recovery corrected and the recovery-corrected results.

The recovery-corrected results of the soil are greater than the consensus values of the proficiency test samples (108 ± 14 %). The consensus values originate from the non-recovery corrected results of 14 laboratories which may have

a negative bias. This illustrates that non-recovery corrected data will typically underestimate the actual value.

Conclusions:

Statistical data treatment demonstrates there is no evidence of significant difference between recovery of natives and their corresponding surrogates. This ratifies their similarity and the suitability of using these surrogates for recovery-corrected quantitation. Application of isotope dilution (recovery correction) technique for PAHs quantitation provides more accurate results than traditional internal standard method for all matrices studied but has a greater influence as the negative bias increases (i.e., soil and diesel emission samples). Isotope dilution should be considered to avoid the impact of bias in quantitation.

References:

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