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Application Note: 30126

Fast GC/HRMS Quantification of 16 EC Priority PAH Components

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Key Words

- DFS
- Food Analysis
- HRGC/HRMS
- Quantitation

Introduction

The European Commission Regulation (EC) No 208/2005 of February 4, 2005, which came into force on April 1, 2005, provides maximum levels for benzo[a]pyrene in different groups of food of which have the strongest regulation foods for infants and young children with max. 1.0 µg/kg and smoked meats and smoked meat products with max. 5.0 µg/kg[1].

The best characterized carcinogenic compound benzo[a]pyrene is used as leading substance out of about 250 different compounds which belong to the PAH group. The German revision of the flavour directive of Mai 2, 2006 (Aromenverordnung) regulates the maximum level for benzo[a]pyrene at 0.03 µg/kg for all types of food with added smoke flavourings.

The Commission Recommendation of February 4, 2005 on the further investigation on the levels of polycyclic aromatic hydrocarbons in certain types of food is directed to analyse the levels of 15 PAH compounds which are classified as priority (see Figure 1) and to check the suitability of benzo[a]pyrene as a marker[2].

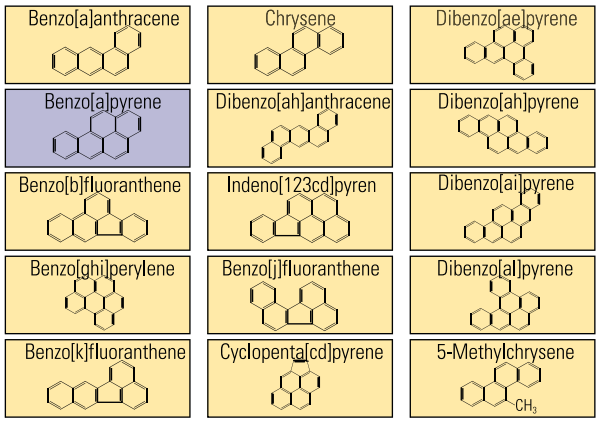

Figure 1: 15 PAH priority compounds classified by the European Commission regulation.

In addition, the Joint FAO/WHO Experts Committee on Food Additives (JECFA) identified the PAH compound benzo[c]fluorene as to be monitored as well[3] see Figure 2.

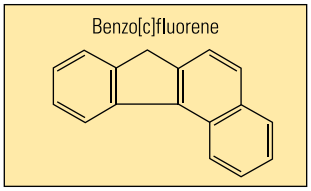

Figure 2: Additional PAH priority compound to be monitored according to JECFA[2].

During GC/MS method setup it turned out that single quadrupole desktop MS instruments could not provide the necessary selectivity at the low decision level[4,5].

The quantitation was done using isotope dilution technique by the addition of isotopically labeled and fluorinated standards before extraction, as well as for the determination of the response factors of all PAH under investigation, see Table 3. Recovery values have been determined by the addition of three ^{2}H labelled compounds, see Table 4.

Analytical Method

The clean-up applied use three steps of pressurized solvent extraction (PSE) for extraction of the lipophilic substances, followed by size exclusion chromatography for the separation from higher molecular substances, and finally a solid phase extraction to remove polar substances.

Experimental Conditions

All measurements were carried out on the Thermo Scientific DFS High Resolution GC/MS system coupled to a Thermo Scientific TRACE GC Ultra™ gas chromatograph equipped with a split/splitless injector. Samples were injected using the Thermo Scientific TriPlus™ Autosampler.

Pressurized solvent extraction (PSE): The homogenized sample (4-6 g meat product, 1-2 g spice) was levigated with the same amount of the drying material poly(acrylic acid), a partial sodium salt-graft-poly(ethylene oxide).

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The resulting material was poured into 33-mL cells, which were locked with glass microfiber filters at the outlet end of the extraction cells. 50 µL of a PAH standard mixture containing the isotope labelled (^{13}C and ^{2}H) and fluorinated PAH compounds were added. The extraction was performed using an ASE 200 unit (Dionex, Sunnyvale, USA) and carried out with n-hexane at 100 °C and 100 bar with a static time of 10 min. The flush volume was 60% and the purge time 120 s. Two static cycles were accomplished. The solvent of the extract was evaporated in a water bath (40 °C) using a nitrogen stream.

Gel permeation chromatography (GPC): The evaporated ASE extract was dissolved in 4.5 mL cyclohexane/ethylacetate (50:50 v/v) and filtered through a PTFE filter with a pore size of 1 µm. The GPC column (25 mm i.d.) was filled with Bio-Beads S-X3 (height of filling 42 cm). Samples were eluted at a flow rate of 5 mL/min with cyclohexane/ethylacetate (50:50 v/v) (dump time 0-36 min, collect time 36-65 min). The solvent was removed with a rotary evaporator, and the eluate was dried in a nitrogen stream.

Solid phase extraction (SPE): This clean-up step to remove more polar substances was performed automatically with a modified ASPEC Xli[6]. This system was modified with a fitting rack, teflon funnels and teflon tubes. Silica, dried for 12 h at 550 °C, was deactivated with 15% water. 1 g dried deactivated silica was filled into commercial 8-mL SPE columns (12 mm i.d.). After conditioning of the columns with 3 mL cyclohexane the samples were applied and eluted with 10 mL cyclohexane.

Preparation for GC/MS analysis: The dried eluate of SPE was dissolved in 1 mL isooctane and 50 µL of the PAH recovery standard mixture (benzo[a]anthracene-d_{12} and benzo[a]pyrene-d_{12} in isooctane) and transferred to a 1 mL tapered vial. The sample was carefully concentrated in a nitrogen stream to a volume of about 50 µL.

GC Parameters	
Injector:	Split/splitless, 1 min, 320 °C, 1.5 µL injection volume with Merlin seal
Carrier gas:	He, 0.6 mL/min, const. flow
Column:	TRACE™-50MS, 10 m x 0.1 mm x 0.1 µm
Oven Temp. Program:	140 °C, 1 min
	10 °C/min to 240 °C
	5 °C/min to 270 °C
	30 °C/min to 280 °C
	4 °C/min to 290 °C
	30 °C/min to 315 °C
	3 °C/min to 330 °C
MS Interface Temperature:	transfer line 300 °C ion source 280 °C

Table 1: GC parameters.

MS Parameters	
Ionization:	EI, 45 eV pos.
Scan Mode:	Multiple ion detection mode (MID)
Resolution:	8,000, 10% valley definition
Cycle Time:	0.8 s/scan

Table 2: MS parameters.

PAH	PAH shortform	Exact mass native [u]	PAH ISTD	Exact mass labelled [u]
Benzo[c]fluoren	BcF	216.0939	5-F-BcF	234.0845
Benzo[a]anthracen	BaA	228.0939	$^{13}C_6$-BaA	234.1140
Chrysen	CHR	228.0939	$^{13}C_6$-CHR	234.1140
Cyclopenta[cd]pyrene	CPP	226.0783		
5-Methylchrysene	5MC	242.1096	d_3-5MC	245.1284
Benzo[b]fluoranthene	BbF	252.0939	$^{13}C_6$-BbF	258.1140
Benzo[j]fluoranthene	BjF	252.0939		
Benzo[k]fluoranthene	BkF	252.0939	$^{13}C_6$-BkF	258.1140
Benzo[a]pyrene	BaP	252.0939	$^{13}C_4$-BaP	256.1037
Indeno[123cd]pyren	IcP	276.0939	d_{12}-IcP	288.1692
Dibenzo[ah]anthracene	DhA	278.1096	d_{14}-DhA	292.1974
Benzo[ghi]perylene	BgP	276.0939	$^{13}C_{12}$-BgP	288.1341
Dibenzo[al]pyren	DlP	302.1096	13-F-DlP	320.1001
Dibenzo[ae]pyren	DeP	302.1096	$^{13}C_6$-DeP	308.1297
Dibenzo[ai]pyren	DiP	302.1096	$^{13}C_{12}$-DiP	314.1498
Dibenzo[ah]pyren	DhP	302.1096		

Table 3: Exact masses of PAH and labeled internal standards.

PAH for recovery standard		Exact mass labelled [u]
Benzo[a]anthracen	d_{12}-BaA	240.1692
Benzo[a]pyrene	d_{12}-BaP	264.1692
Benzo[ghi]perylene	d_{12}-BgP	288.1692

Table 4: Exact masses of PAH recovery standards.

RT	Exact mass [min]	Function [u]	Dwell time [ms]
8:50	216.09375	native	82
	218.98508	lock	2
	226.07830	native	82
	228.09383	native	82
	234.08450	native	82
	234.11400	native	82
	240.16920	native	82
	263.98656	cali	6
13:00	218.98508	lock	2
	242.10960	native	82
	245.12840	native	82
	252.09390	native	82
	256.10730	native	82
	258.11400	native	82
	263.98656	cali	6
	264.16920	native	82
19:00	263.98656	lock	2
	276.09390	native	74
	278.10960	native	74
	288.13410	native	74
	292.19740	native	74
	313.98340	cali	6
22:00	263.98656	lock	2
	302.10960	native	120
	308.12970	native	120
	313.98340	cali	6
	314.13980	native	120
	320.10010	native	120

Table 5: MS parameters with MID descriptor for PAH Fast GC/HRMS data acquisition.

Results

The initial use of a 50% phenyl capillary column of 60 m length (60 m x 0.25 mm x 0.25 µm, at constant pressure) provided the required chromatography resolution for the various isomers. The necessary retention time of more than 90 min turned out to be not appropriate for a control method with high productivity.

The application of fast GC column technology reduced the required retention by 3/4 to only 25 min maintaining the necessary isotope resolution, see Figure 3. The critical separation components are shown in detail in Figure 4 a-c. For all components the fast GC method provides a robust peak separation for a quantitative peak integration.

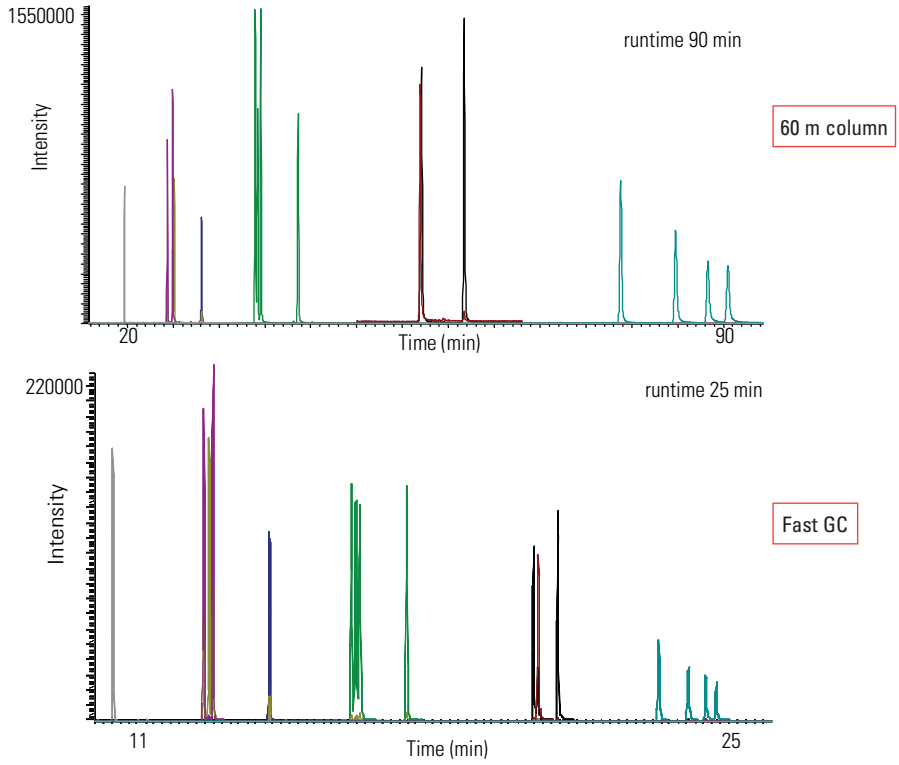


Figure 3: Top: Regular GC separation, 60 m column, > 90 min retention time. Bottom: Fast GC separation, 10 m column, approx. 25 min retention time.

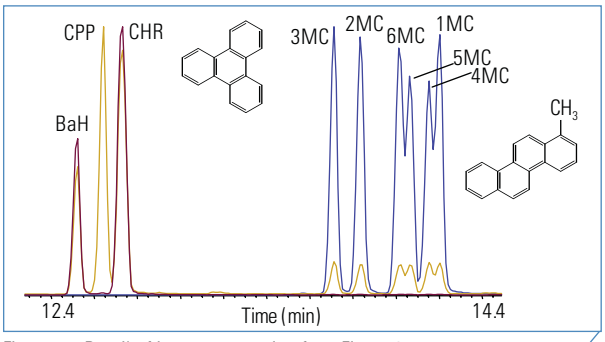


Figure 4a: Detail of isomer separation from Figure 3.

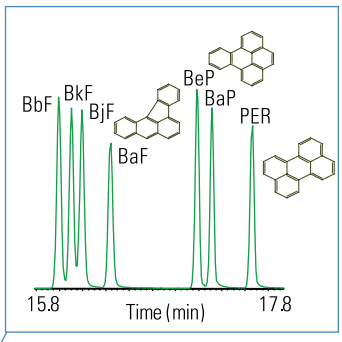
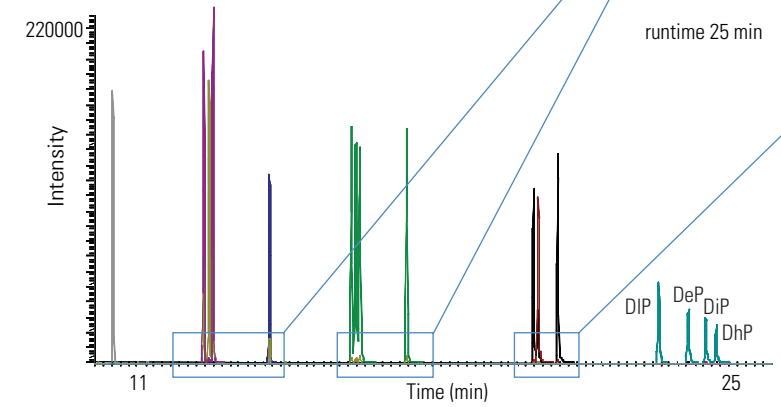


Figure 4b: Detail of isomer separation from Figure 3.



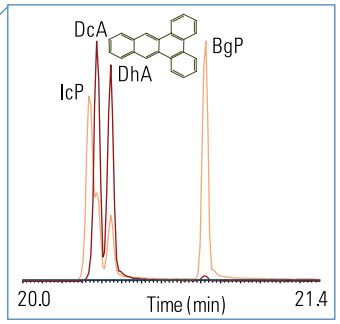


Figure 4c: Detail of isomer separation from Figure 3.

Figure 4: Fast GC separation with zoom.

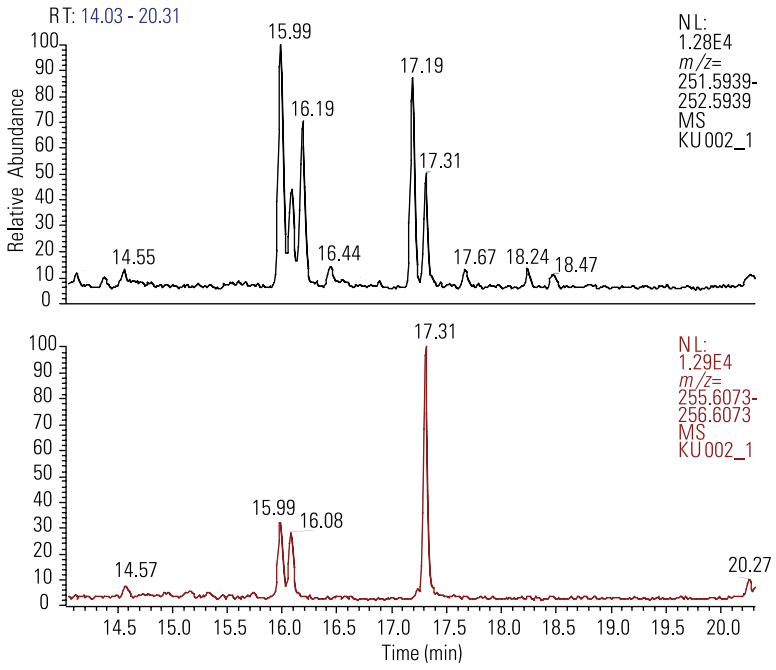


Figure 5: Benzo[a]pyrene determination (RT 17:31 min) in caraway seeds at a level of 0.02 µg/kg (max. concentration 0.03 µg/kg incorporated by the addition of spices), elution sequence BbF, BkF, BjF, BeP, BaP, top native PAH, bottom ^{13}C-BaP.

Sample Measurements

Applicability for different matrices has been shown especially for those matrices known to be critical in this type of analysis. Figure 5 shows the analysis of the extract from caraway seeds with a determined concentration of benzo[a]pyrene of 0.02 µg/kg. An LOD of 0.005 µg/kg and an LOQ of 0.015 µg/kg can be estimated for the analysis of spices, when the sample weight is 1 to 1.5 g. The recovery values achieved with the described sample preparation has been between 60 and 120%.

Conclusions

The retention time of of more than 90 minutes for regular chromatography conditions was successfully reduced to approximately 25 minutes maintaining chromatographic resolution. In practice the fast GC separation combined with a high resolution GC/MS detection system has proven to be a fast and reliable quantitation of PAH at the legally required level in routine analysis.

References

[1]COMMISSION REGULATION (EC) No 208/2005 of 4 February 2005 amending Regulation (EC) No 466/2001 as regards polycyclic aromatic hydrocarbons.

[2]COMMISSION RECOMMANDATION of 4 February 2005 on the further investigation into the level of polycyclic aromatic hydrocarbons in food.

[3]Summary and Conclusion of the Joint FAO/WHO Expert Committee on Food Additives, Sixty-Fourth meeting, Rome, 8-17 February 2005, JCEFA/64/SC.

[4]Ziegenhals, K., Jira, W., High sensitive PAH method to comply with the new EU directives, Presentation at the European High Resolution GC/MS Users Meeting, Venice, Italy, March 23 -24, 2007.

[5]Ziegenhals, K., Jira, W., Bestimmung der von der EU als prioritär eingestuften polyzyklischen aromatischen Kohlenwasserstoffe (PAK) in Lebensmitteln, Kulmbach Kolloquium, Sept. 2006.

[6]Kleinhenz, S., Jira, W., Schwind, K.-H.: Dioxin and polychlorinated biphenyl analysis: Automation and improvement of clean-up established by example of spices, Molecular Nutrition & Food Research 50 (4-5) (2006) 362-367.

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Application Note: 10170

Ultra Fast GC Method for the Analysis of Total Hydrocarbons in Water in Compliance with ISO 9377-2 (Mod.)

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Key Words

- Oil in Produced Water
- ISO 9377-2 (Mod.)
- Hydrocarbons nC7-nC40
- BTEX
- Ultra Fast GC

Introduction

Several million tons of water containing petroleum hydrocarbons are produced every year by offshore plants in the extraction process of oil and gas from undersea. The discharge of such produced water into the ocean is regulated by severe norms in order to protect the environment from pollution. The Oslo and Paris Commission (OSPAR) is responsible for the decisions and recommendations concerning marine issues in the North East Atlantic area, and sets the reference analytical methods for monitoring the pollutants content in produced water before discharge.

The OSPAR commission has recently confirmed that, starting from January 2007, a modification of the ISO 9377-2, indicated as ISO 9377-2 (Mod.) [1], will be the new reference method for the determination of oil in produced water.

This is a GC-based method, whose goal is to determine the level of pollution in water expressed with the "Hydrocarbon Index" (HI), corresponding to the cumulated amount of hydrocarbon compounds.

Stringent regulations regarding the use of toxic extraction solvents, such as CCl_4, TTCE, or Freon make alternative Infra Red methods less favorable. Freon has been banned by the Montreal Protocol, due to its ozone depleting properties, and TTCE has not been fully accepted, due to its suspected carcinogenic effects.

In this application, Ultra Fast GC [3,4] is demonstrated as a reliable GC technique able to fulfill the strict requirements of the ISO 9377-2 (Mod.), featuring analysis time comparable to that of the IR methods. Productivity is increased by a factor of 10 in comparison with conventional GC, using a very simple and rugged hardware.

Experimental

Official norm and sample preparation

The ISO 9377-2 defines the HI as the cumulated amount of hydrocarbons included in the range between n-C10 and n-C40, to be analyzed in 4 different steps:

a) extraction of the hydrocarbons from the sample matrix with an organic solvent;

b) clean-up with Florisil® in order to remove the more polar substances;

c) re-concentration of the extract through solvent evaporation;

d) GC-FID analysis of the cleaned concentrated extract.

Some correlation data have clearly pointed out that ISO 9377-2 underestimates the dispersed oil content in water, compared with the IR reference method, and the main reason lies in the too narrow range of hydrocarbons investigated through this GC method [2].

For this reason the OSPAR commission basically decided to propose a few modifications to the ISO 9377-2, to generate the ISO 9377-2 (Mod.) as a new reference in replacement of IR based methods [1].

The new reference implies a broader range of investigation, from n-C7 to n-C40, and the use of n-pentane as extraction solvent. Since Toluene, Ethylbenzene and Xylenes do elute in this range, but are not considered part of the dispersed (aliphatic) oil in water, their content has to be calculated and subtracted from the hydrocarbons value.

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Another important modification concerns the re-concentration step, that has to be completely by-passed: the GC system must be sensitive enough to directly analyze the extract content with no solvent evaporation before the analysis. This will allow for a faster sample prep, and will prevent any risk of losing volatiles during the solvent evaporation step.

Here is the summary of the main modifications reported in ISO 9377-2 (Mod.):

- use of n-pentane as extraction solvent;
- spike the sample with n-C7 and n-C40;
- integrate the group peak in the range nC7-nC40;
- integrate the TEX peaks and subtract their areas from the group peak, in order to calculate the dispersed oil content.

Sensitivity issue: the system has to allow the determination of 0.1 mg/L of hydrocarbons in the water sample, corresponding to about 2 mg/L in the water extract, avoiding any re-concentration step.

Instrumentation and Data System

A Thermo Scientific TRACE GC Ultra™ equipped with the Ultra Fast Module (UFM) option, featuring a Programmable Temperature Vaporizing (PTV) inlet / FID configuration was used. Injections were performed with the Thermo Scientific TriPlus™ Autosampler. The UFM option consists of a column module (Fig. 1) containing a capillary column combined with a heating element and a temperature sensor to ensure the direct resistive heating of the capillary column [3]. The assembly is held in an "easy to handle" metal cage and can achieve temperature programming rates as high as 1200 °C/min.

The column module can be installed and removed from a standard GC oven as easily as a normal capillary column, offering the benefit of a 3-4 times longer average lifetime. The reason for this plus is that in Ultra Fast GC the column usually spends far shorter time at the upper isothermal temperature, in comparison with conventional temperature programs.

For this method, the Ultra Fast GC column module was equipped with a 5 m, 0.1 mm i.d., 0.1 µm film thickness UF-1 column (non-polar phase, Thermo Scientific).

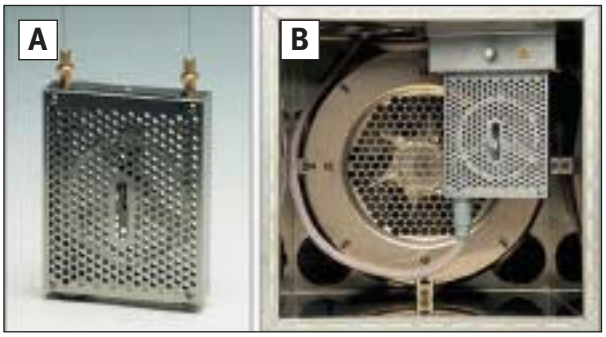


Figure 1: UFM column module (A) and its housing in a TRACE GC Ultra oven (B).

The injector is a PTV, able to grant high recoveries for broad ranges of boiling points, avoiding any discrimination from the syringe needle during the injection phase. The sample is injected into the cold inlet as a liquid, and is then vaporized in the middle zone through the very fast heating of the injector body (at 14 °C/sec) [5].

The sample vapors are then carried into the column module: the interface zone of the column is permanently heated through a metal block to prevent any risk of cold spot formation. The inlet temperature profile has been properly optimized (Fig. 2) to allow the coexistence of a cold-heated middle zone and a permanently heated one, within the same injector.

The relatively low thermal mass of this injector allows rapid cooling carried out through a dedicated fan. No external coolant other than ambient air is needed.

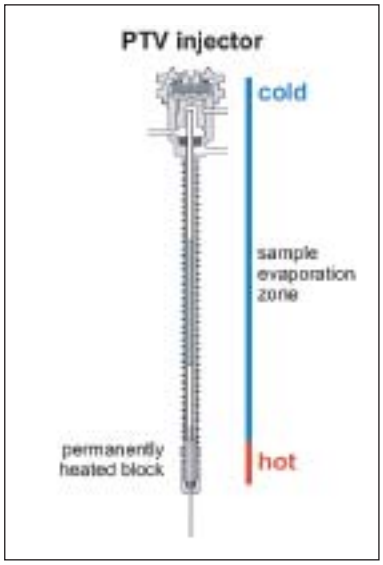


Figure 2: PTV inlet temperature profile.

Thermo Scientific Chrom-Card software incorporates a dedicated function that allows the automatic integration of the portion of the chromatogram included between the retention times of n-Heptane (C7) and n-Tetracontane (C40), into a single group area, with the baseline reported at the signal level in front of the solvent peak. The integration of the individual TEX peaks is automated as well, so that one single analytical report includes both the group peak area and the TEX peak areas.

Standard mixtures for evaluating injection performances were prepared diluting n-alkanes, ranging from *n*-C7 to *n*-C40, in n-pentane at ppm levels. A Gasoil Reference Mix diluted in n-pentane was analyzed at different concentrations to test linearity, repeatability and sensitivity of the method. Several real water extracts have been analyzed to test the robustness of the described GC system.

Ultra fast analysis: results and discussion

For all the ultra fast analyses discussed in this paragraph, the column temperature is programmed from 35 °C (0.8 min) to 350 °C (0.4 min) at 100 °C/min.

3 µL have been injected in split mode (split flow: 10 mL/min).

0.5 µL of MTBE has been injected as a Co-solvent in order to enhance the solvent effect and optimize the recovery of the more volatile compounds.

(In all the chromatograms shown, the position of nC7 and nC40, when not present in the samples, is reported in dotted lines).

System compliance test

A solution of hydrocarbons has been analyzed in order to verify the baseline separation of C7 from n-pentane, which is easily observed (Fig. 3), and then to confirm the absence of any discrimination effect: under the analytical conditions indicated, the peak area ratio C40/C20 has been found to be > 0.9, far higher than the minimum value (0.80) requested by ISO 9377-2 (Mod.) to consider the injector as not discriminating.

This is one of the most demanding parameters for the injection system to obtain compliance with the official norm.

The same analysis demonstrates the ability of separating TEX components, even better shown in the analysis reported in Fig. 4.

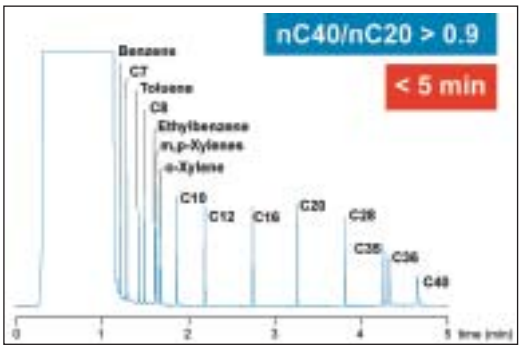


Figure 3: Standard chromatogram nC7–nC40.

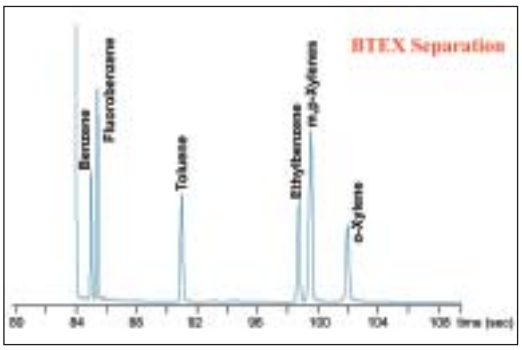


Figure 4: Standard chromatogram with TEX.

Fig. 5 shows the chromatogram of a Gasoil Reference Mix, 50 ppm of total hydrocarbons (high-lighted the separation C17-Pristane and C18-Phytane).

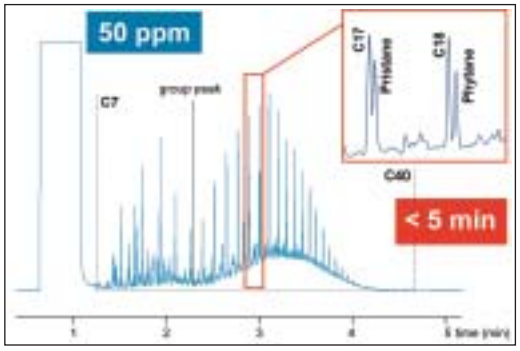


Figure 5: Gasoil Reference Mix, 50 ppm.

Linearity and repeatability

Linearity has been tested by injecting the reference gasoil mixture at different concentrations (2-200 ppm), getting an excellent linear coefficient (Fig. 6).

The RSD % of the group peak, calculated over 10 consecutive repetitions of the reference at 50 ppm, is around 2 %.

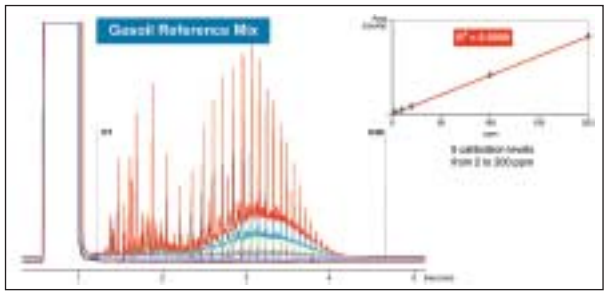


Figure 6: Linearity Test: 5 overlaid chromatograms and linear curve.

Sensitivity test

Ultra Fast GC is able to produce a peak compression effect as a consequence of operating at high heating rates with short narrow-bore columns. The signal-to-noise ratio is maximized, and the outcome is an increase in sensitivity over conventional GC by a factor that depends on the heating rate applied: the higher the heating rate, the higher the overall sensitivity delivered.

Fig. 7, reporting the chromatogram of the reference gasoil mix at 2 ppm, overlapped with that of the blank (n-pentane), proves that the system is as sensitive as requested by the method, with no need to inject more than 3 µL.

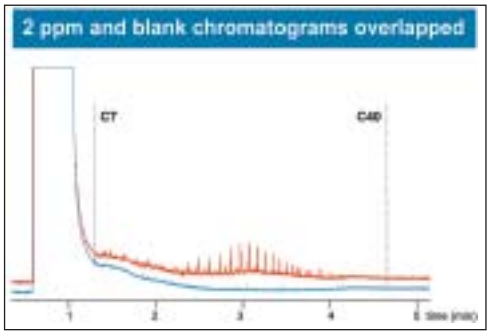


Figure 7: Sensitivity test.

System robustness

A new liner model was used, pre-packed with a glass wool layer located on top of a glass restriction in order to prevent contamination of the column by non-volatile components (Fig. 8). The restriction keeps the wool in the same position in the liner, improving the repeatability of the results.

To prove the system robustness, a large number of real water extract samples (about 100) was injected (Fig. 9) without replacing neither the liner nor the glass wool, and a reference mix was analyzed a few times before and after the long sequence: the high level of repeatability of these analyses (still around 2-3 %) and nice chromatograms shape prove (Fig. 10) that neither column contamination nor degradation of chromatographic performance occurred.

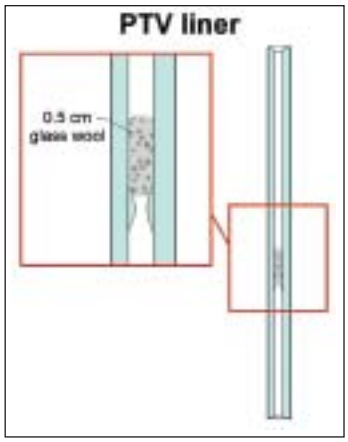


Figure 8: PTV liner model with glass wool.

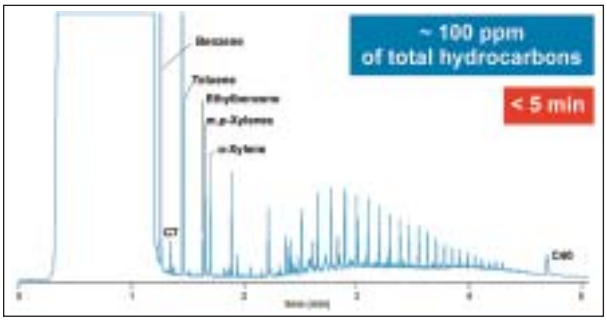
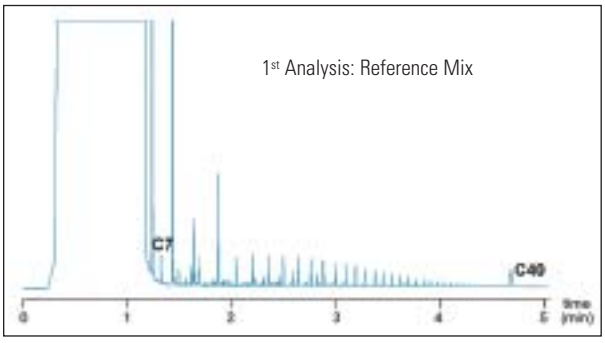


Figure 9: Real water extract chromatogram.

Overall productivity

The productivity of this Ultra Fast method can be easily calculated through the number of samples per day that can be potentially analyzed. Besides the run time, around 4.5 minutes, even the column cooling time is extremely fast, being around 2 minutes.

So, the resulting run-to-run time is about 8 minutes, which leads to a total productivity of about 60 samples per day, not including the runs that could be performed unattended overnight.



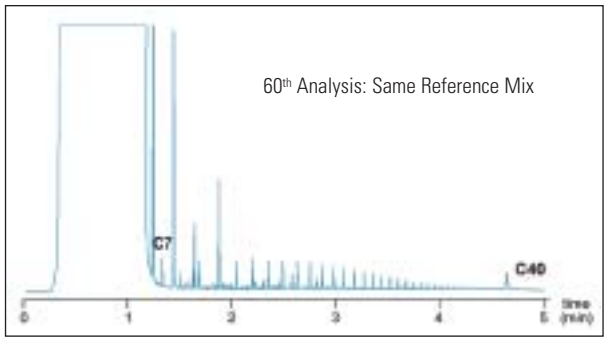


Figure 10: First and last analysis of a 1-day sequence.

Conclusion

The OSPAR commission, that regulates the discharge of produced water in the North Sea, has confirmed that the ISO 9377-2 (Mod.) will be the new reference GC-based method for the determination of the Hydrocarbon Index, starting from January 2007, in replacement of the IR reference method.

The Ultra Fast option of the TRACE GC Ultra has proven to accomplish this determination in full compliance with the strict requirements of the new official norm, cutting the analytical time by a factor of 10 with respect to conventional GC.

Impressive lab productivity is delivered through a very simple and rugged hardware, quite suitable for the analyses of very dirty matrices usually requested in this field.

Low frequency of maintenance, extreme ease of use of the data system provided with a dedicated turn-key method, and high level of automation: these further features position the described technique as the ideal solution for quickly delivering hydrocarbons analysis in water according to ISO 9377-2 (Mod.).

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5. R. Facchetti, T. Porzano, A.Cadoppi and P. Magni, Proceedings of 27th International Symposium of Capillary Chromatography, M17, Riva del Garda, Italy, May 31 – June 04, 2004, ed. P. Sandra.

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AN10170_E 12/07C

Application Note: 10137

Ultra Fast GC Method for the Analysis of Total Petroleum Hydrocarbons (TPH) in Water and Soils, in Compliance with Texas TNRCC 1005

Thermo Fisher Scientific, Milan, Italy

Key Words

- TRACE GC Ultra
- Texas TNRCC 1005
- Total Petroleum Hydrocarbons
- Ultra Fast GC
- Water and Soil Analysis

Figure 1: TRACE GC Ultra™ with TriPlus™ AS Autosampler

Introduction

As attested by a US EPA survey, since over 20 years ago, hundreds of thousands of underground storage tanks (USTs) leaking petroleum have contaminated worldwide community drinking water supplies [1].

Recent regulations affecting both drinking water suppliers and environmental protection institutes of many European and US countries have made the determination of the content of mineral oils and petroleum products in water and soils a compulsory requirement for quality certifications.

Currently, the analytical techniques used to carry out this determination are Infra Red and Gas Chromatography. IR, although it has been extensively used in the past for its simplicity and high speed of analysis, implies the mandatory use of CCl_4, TTCE, or Freon as the extraction solvent, which is not favorable. CCl_4 is currently banned due to its tremendous toxicity; Freon has been banned by the Montreal Protocol (1992), due to its ozone-depleting properties; TTCE has not been fully accepted, since the concern about its suspected carcinogenic effects.

In this light, GC-FID, being a robust technique and featuring no limitations in the solvent selection, emerges as the most valid alternative technique tolerated and supported by official norms for total petroleum hydrocarbons (TPH) applications. One of these norms, TNRCC 1005 from the Texas Commission on Environmental Quality (formerly Texas Natural Resource Conservation Commission) [2], has shown good correlation with IR-based method EPA 418.1, and is widely applied not only in Texas but throughout the United States.

This application is based on sample extraction with *n*-pentane and GC-FID monitoring of the hydrocarbon range from nC6 to nC36. This application shows the details of a new Ultra Fast GC method for TPH, able to comply with TNRCC 1005, and to compete with IR on analysis time; productivity is increased by a factor of 10 in comparison with conventional GC using a very simple and rugged hardware [6,7].

Experimental

Official norm and sample preparation

The TNRCC 1005 method consists of 2 consecutive steps:

1) in-vial extraction of the hydrocarbons from the sample matrix with *n*-pentane;
2) GC-FID analysis of the extract

About 10 mL of sample have to be extracted with 3 mL of *n*-pentane directly in a vial, and an aliquot of the extract will be analyzed by a GC unit, properly calibrated by means of diluted gasoil external standards ranging from 20 to 1000 ppm as a total hydrocarbons content. The TPH content will be calculated by integrating a group peak from nC6 to nC36, added as internal standards.

Re-concentration of the extract before the GC analysis through partial solvent evaporation is not admitted, and the GC system must be sensitive enough to directly analyze the extract content avoiding any solvent evaporation before the analysis. This allows for much faster and cheaper sample prep and prevents any risk of losing volatiles during the solvent evaporation step.

Sensitivity issue: the GC method must be able to quantify at least 5 ppm (mg/Kg) of TPH in the extract.

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The official method reports that the GC analysis can be achieved using a non-polar column (25-30 m long, 0.25 mm as internal diameter, and film thickness ranging from 0.25 to 1 µm), oven temperature program from 30 to 325 °C operated at a heating rate of 15 °C/min, for a total analysis time around 30 minutes. But in the method text itself it is remarked that these parameters are only recommended; any changes to these method conditions can be made by the analyst in order to improve speed of analysis, sensitivity, separation, or to reduce the cost per analysis, providing that the new parameters will still provide compliance with the analytical goals.

Instrumentation and data system

A Thermo Scientific TRACE GC Ultra™ (Figure 1), equipped with the Ultra Fast Module (UFM) option, featuring a Programmable Temperature Vaporizing (PTV) inlet / FID configuration was used. Injections were performed with the TriPlus Autosampler (Thermo Electron). The UFM option consists of a column module (Figure 2) containing a capillary column combined with a heating element and a temperature sensor to ensure the direct resistive heating of the capillary column [3,4]. The assembly is held in an "easy to handle" metal cage and can achieve temperature programming rates as high as 1,200 °C/min.

The column module can be installed and removed from a standard GC oven as easily as a normal capillary column, offering the benefit of a 3-4 times higher average lifetime. The reason for this added longevity is that, in Ultra Fast GC, the column spends a far shorter time at the upper isothermal temperature in comparison with conventional temperature programs.

For this method, the Ultra Fast GC column module was equipped with a 5 m, 0.32 mm i.d., 0.5 µm film thickness Thermo Scientific TRACE™ UFC-1 column (P/N UFMC00001070907).

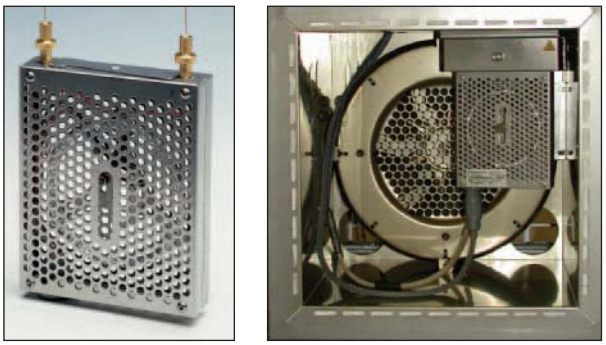

Figure 2: UFM column module[A] and its housing in a TRACE GC Ultra oven [B].

The injector is a PTV, able to grant high recoveries for broad ranges of boiling points, avoiding any discrimination from the syringe needle during the injection phase. The sample is injected into the cold inlet as a liquid, and is then vaporized in the middle zone through the very fast heating of the injector body (at 14 °C/sec) [5].

The sample vapors are then carried into the column module. The interface zone of the column is permanently heated through a metal block to prevent any risk of cold spot formation. The inlet temperature profile has been properly optimized (Figure 3) to allow the coexistence of a cold-heated middle zone and a permanently heated zone, within the same injector.

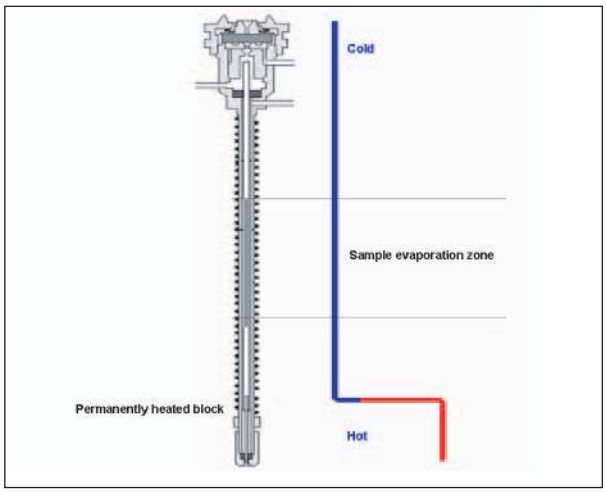

Figure 3: PTV inlet temperature profile

Thermo Scientific Chrom-Card software incorporates a dedicated function that allows for automatic integration as a single group area the portion of chromatogram included between the retention times of *n*-Hexane (nC6) and *n*-HexaTriacontane (nC36), with the baseline reported at the signal level in front of the solvent peak.

Standard mixtures for evaluating injection performances were prepared diluting *n*-alkanes, ranging from *n*-C6 to *n*-C40, in *n*-pentane at ppm levels. The Gasoil Reference D2887 diluted in n-pentane was analyzed at different concentrations to test linearity, repeatability, and sensitivity of the method. Several real water extracts have been analyzed to test the robustness of the described GC system.

Ultra fast analysis: results and discussion

For all the ultra fast analyses discussed in the paragraph below, the column temperature is programmed from 5 °C (0.5 min) to 110 °C at 180 °C/min, then at 160 °C/min to 330 °C (0.3 min).

The initial temperature of 5 °C is obtained using a cryogenic coolant (Liquid N_2 or Liquid CO_2) in the oven chamber. This allows for an enormous increase in the overall number of theoretical plates, thereby achieving the high resolution power needed to separate nC6 from *n*-pentane [6]. An injection of 1 µL was made, using split mode, split ratio 1:4. All of the chromatograms presented have been obtained in less than 3 minutes.

System compliance test

A first analysis of a solution of *n*-alkanes has been performed in order to verify the baseline separation of C6 from *n*-pentane, which is easily observed (Figure 4), and then to check for absence of any discrimination effects. Under the analytical conditions indicated, even nC40 is eluted with excellent recoveries (the actual limit indicated in TNRCC 1005 is nC36).

A different standard has been analyzed to demonstrate that the resolution is high enough to even separate TEX components, in case they are present (Figure 5). The position of n-C6 and n-C8 alkanes is reported with dotted lines.

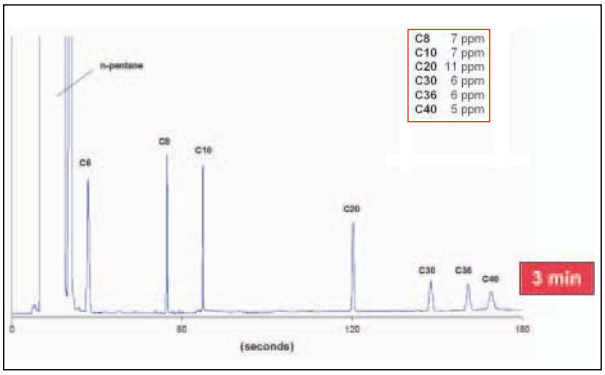

Figure 4: Standard chromatogram nC6–nC40

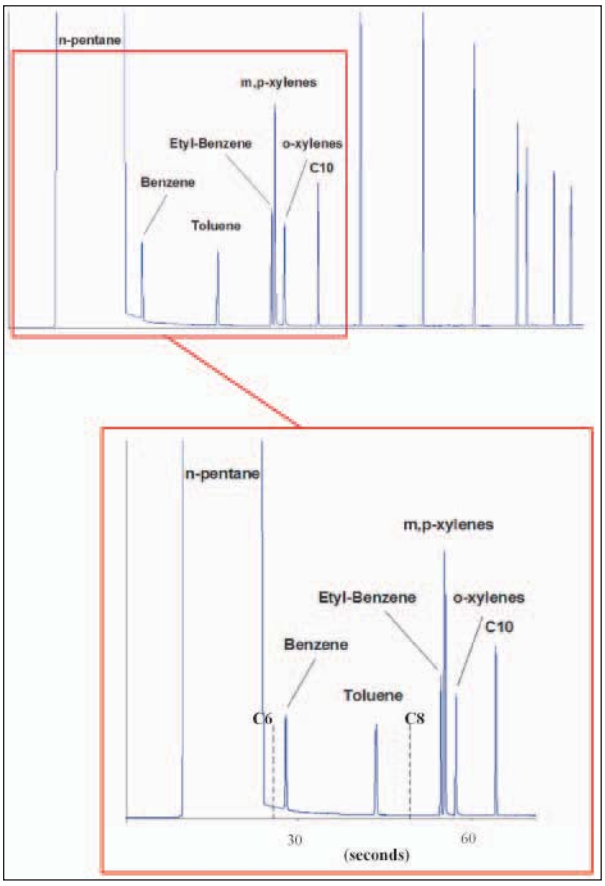

Figure 5: Standard chromatogram with TEX

Linearity and repeatability test

Linearity has been tested by injecting the Gasoil D2887 reference mixture at different concentrations (20-1000 ppm), getting an excellent linear coefficient (Figure 6). The %RSD of the group peak, calculated over 10 consecutive repetitions of the D2887 reference at 50 ppm (Figure 7), was 2.8%.

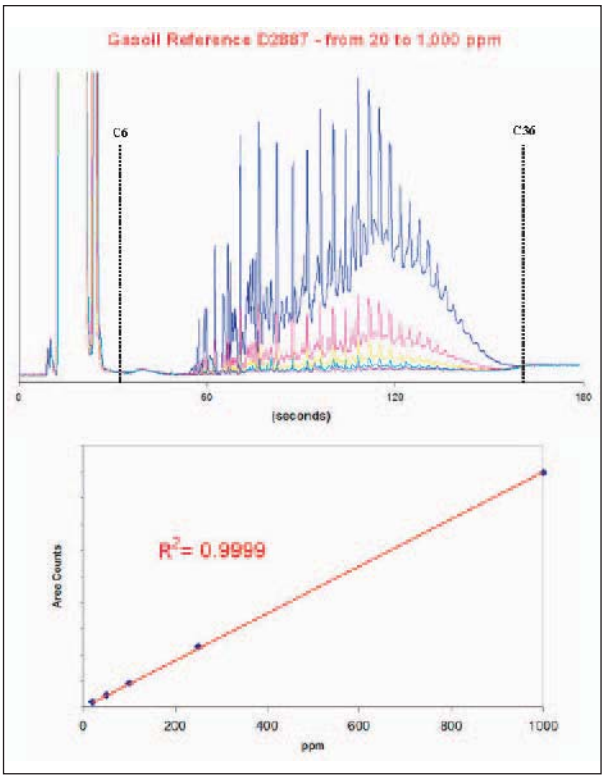

Figure 6: Linearity Test: 5 overlaid chromatograms and linear curve

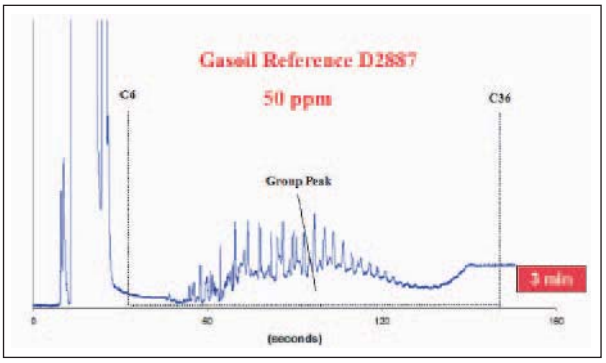

Figure 7: Gasoil Reference D2887 analysis

Sensitivity test

Ultra Fast GC is able to produce a peak compression effect as a consequence of operating at high heating rates with short columns. The signal-to-noise ratio is maximized, and the outcome is an increase in sensitivity over conventional GC by a factor that depends on the heating rate applied: the higher the heating rate, the higher the overall sensitivity delivered.

The system has proven to be as sensitive as requested by the norm, being able to quantify 5 ppm of total hydrocarbons in n-pentane with no need to inject more than 1µL.

In fact, the D2887 Reference diluted to 5 ppm in *n*-pentane was analyzed using the described parameters, and the ratio between the reference group peak area and the solvent (blank) area, analyzed under the same conditions, was 4.9. All the chromatograms are automatically baseline corrected by the data system.

System robustness

A plug of glass wool was placed in the middle part of the liner in order to prevent contamination of the column by non-volatile components. To prove system robustness, a large number of real water extracted samples (approximately 100) were injected (see Figure 8) without replacing the liner or the glass wool, and at the end of the sequence the reference mix was analyzed several times. The high level of repeatability of these analyses (still around 2-3 %) proves that neither column contamination nor degradation of chromatographic performance occurred.

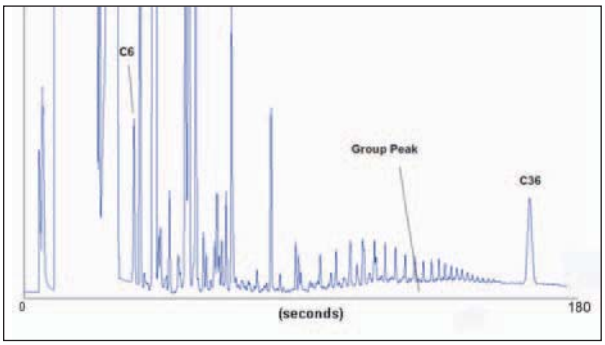

Figure 8: Real water extract chromatogram

Overall productivity

The productivity of this Ultra Fast method can be easily calculated through the number of samples per day that can be potentially analyzed. Besides the run time, around 3 minutes, even the module cooling time is extremely fast, taking only 4 minutes to cover the temperature range from 330 °C (upper isothermal) to 5 °C (initial isothermal). This performance is even faster than a normal GC covering a normal range of temperatures from the upper isothermal to ambient.

The run-to-run time is about 7 minutes, which leads to a total productivity of about 70 samples per day, not including the runs that could be performed unattended overnight.

The sampling time, defined as the time needed by the autosampler to wash the syringe, is not considered, due to the capability of the TriPlus Autosampler of performing the syringe washing cycles during the previous analytical run in the sequence. This eliminates most of the dead times that usually exist between two consecutive runs.

The TriPlus AS has been conceived to boost productivity. The "clone" configuration (see Figure 9) allows for the installation of one autosampler to automate 2 adjacent GCs working simultaneously. In this way, one sampling turret works as two virtual autosamplers, even doubling the overall productivity.

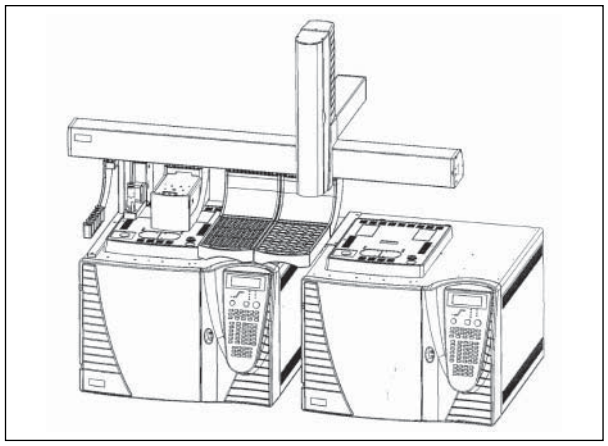

Figure 9: TriPlus AS automating 2 GCs working simultaneously

Conclusions

The Ultra Fast option of the TRACE GC Ultra effectively accomplishes the determination of Total Petroleum Hydrocarbons in water and soil in compliance with the strict requirements of Texas TNRCC 1005, reducing analytical time by a factor of 10 with respect to conventional GC.

Impressive productivity is delivered through simple and rugged hardware, quite suitable for the analyses of dirty matrices usually requested in this field. Low frequency of maintenance, easy-to-use data system provided with a dedicated turn-key method, and high level of automation: these features position the described assembly as an ideal solution for quickly implementing Texas TNRCC 1005 in any environmental laboratory.

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Acknowledgement

Authors: Stefano Pelagatti, Riccardo Facchetti and Andrea Cadoppi

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AN10137_E 09/07C

Application Note: 10209

Analysis of Wastewater for Volatile Organics (EPA Method 8260C) by GC/MS

Jessie Butler, David Steiniger, Eric Phillips, Thermo Fisher Scientific, Austin, TX, USA

Key Words

- DSQ II Single Quadrupole GC/MS
- EnviroLab Forms
- EPA Method 8260C
- Purge and Trap
- Volatile Organics

Overview

United States Environmental Protection Agency (US EPA) Method 8260 is an analytical method for the measurement of volatile organic pollutants in a wide range of matrices from ground water to aqueous sludge, oily waste, and sediment.[1] Method 8260C lists 100 organics with diverse physical properties, from a gas at room temperature, like vinyl chloride, to an aromatic like naphthalene that elutes from the analytical column at 230 °C. There are also very polar compounds, like tert-butanol, and very reactive components such as 2-chloroethyl vinyl ether. In addition, the linear calibration range covers 1 µg/L to 200 µg/L, with detection limits cited in the method at 5 µg/L for ground water, 5 µg/kg for soil, and 0.5 mg/kg for waste oils.[1] These factors present a significant challenge for any instrument and analyst in the environmental laboratory.

The Thermo Scientific 8260 Productivity Solution offers a comprehensive start-up package for the installation of the Thermo Scientific DSQ™ II single quadrupole mass spectrometer, Thermo Scientific FOCUS™ GC, and a purge and trap system in your laboratory as a dedicated analyzer for EPA Method 8260C. For this Productivity Solution, the DSQ II MS and FOCUS GC (Figure 1), along with an OI Analytical Eclipse 4660 Purge and Trap and an OI Analytical 4551 Autosampler, were put through rigorous QC tests to measure the precision, linearity, accuracy, and sensitivity of the entire instrument system for EPA Method 8260C. This application note highlights the performance of the Productivity Solution approach. The results show compliance to all QC tests with a run time of 11 minutes, with an average method detection limit of 0.35 µg/L.

This comprehensive approach to EPA Method 8260C ensures your laboratory's success in the measurement of precision, linearity, accuracy, and sensitivity for the analysis of wastes and wastewater according to the guidelines specified in EPA Method 8260C.

Figure 1: Thermo Scientific DSQ II GC/MS with FOCUS GC

Methods

All standards were prepared in organic-free water as specified in the 8260 Productivity Solution Standard Operation Procedure, *Determining Volatile Organics in Wastewater Using the DSQ II*.[2] Approximately 100 target compounds were analyzed to determine their linear range, method detection limit (MDL), and accuracy and precision of analysis in the method validation (MVD) study. A split injection was made using a purge and trap adapter interface to integrate the concentrator to the GC for sample introduction. The mass spectrometer was operated in EI Full Scan mode. The chromatography was optimized to provide a short run time, with all compounds eluting in less than 11 minutes. The mass spectrometer was tuned using Target Tune to meet the mass resolution criteria for 4-bromofluorobenzene (BFB) as specified in the EPA method.

Results

The 8260 Productivity Solution for the DSQ II GC/MS system was evaluated against the QC criteria for EPA Method 8260C. The results showed compliance to all QC tests set in the method. The linear range was determined to be 1 to 200 µg/L with an average percent relative standard deviation (%RSD) of 6.9. The average MDL was 0.35 µg/L. A total ion chromatogram for a 20 µg/L mid-level standard acquired during the method validation study is shown in Figure 2. Uniformity of spectral identification for detection was ensured by applying tuning compound ion ratio criteria for BFB. Table 1 lists method validation, method detection and calibration results for selected compounds from the 8260C target list. This table includes system performance check compounds, and demonstrates the accuracy, precision, and sensitivity of the method when using the DSQ II system.

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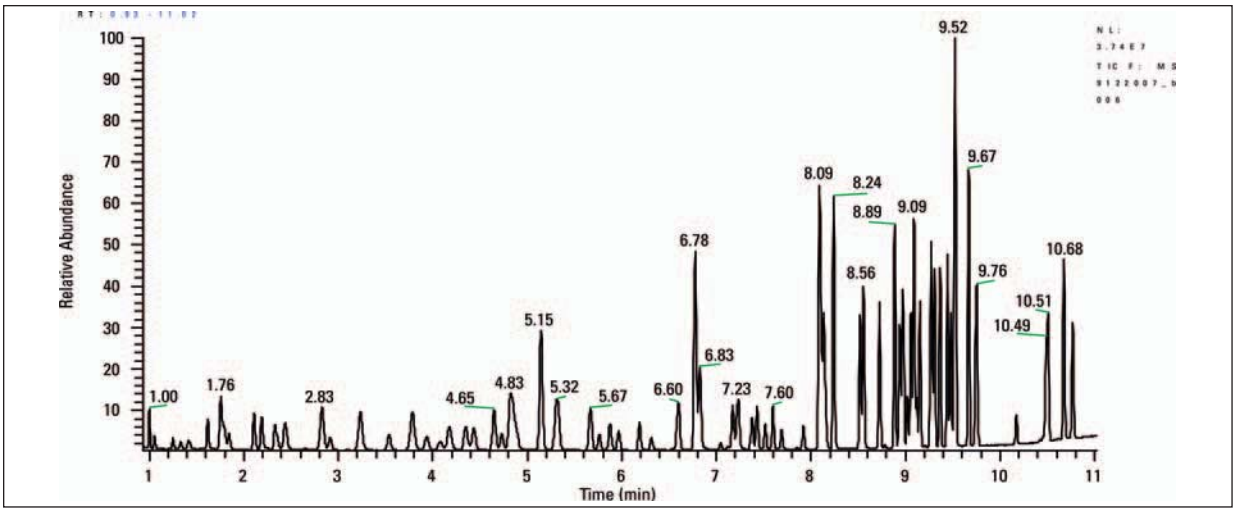

Figure 2: Total ion chromatogram of 20 µg/L method validation standard

	Linearity	Method Validation (MVD)		Method Detection Limit (MDL)
Component	**%RSD**	**% D**	**%RSD**	**(µg/L)**
dichlorodifluoromethane	8	-16.2	6	0.22
chloromethane	5	-3.8	5	0.21
vinyl chloride	12	-10.6	6	0.38
bromomethane	6	-5.0	5	0.38
chloroethane	10	-1.5	5	0.47
trichlorofluoromethane	11	-10.6	6	0.29
carbon disulfide	1	-10.8	6	0.22
1,1,2-trichloro-1,2,2-trifluoroethane	2	-13.9	6	0.37
methyl tert-butyl ether (MTBE)	5	-2.0	2	0.20
tert-butanol	16	29.4	7	1.07
diisopropyl ether (DIPE)	5	-2.7	3	0.49
allyl alcohol	7	-1.4	3	0.28
ethyl tert butyl ether (ETBE)	7	-2.3	3	0.24
benzene	5	-3.3	4	0.21
tert-amyl methyl ether (TAME)	7	1.3	3	0.19
dibromomethane	2	5.5	2	0.14
methyl methacrylate	8	-1.7	2	0.15
2-chloroethyl vinyl ether	6	-2.3	1	0.18
4-methyl-2-pentanone (MIBK)	11	5.7	5	0.70
ethyl methacrylate	10	-1.0	2	0.17
chlorobenzene	3	-0.3	3	0.17
o-xylene	6	0.5	4	0.20
bromoform	7	6.7	2	0.19
bromobenzene	8	3.8	4	0.18
trans-1,4-dichloro-2-butene	4	-1.3	3	0.29
1,3-dichlorobenzene	6	2.1	3	0.14
benzyl chloride	9	5.5	5	0.33
1,2-dibromo-3-chloropropane	9	1.7	4	0.30
naphthalene	9	12.3	3	0.35
1,2,3-trichlorobenzene	9	10.1	4	0.37

Table 1: Method linearity, validation, and detection limit study results for selected 8260C compounds

Conclusions

The 8260 Productivity Solution provides fast chromatography, with the last target compound eluting at less than 11 minutes. The DSQ II system successfully met the QC criteria for EPA Method 8260C in a split mode of injection using the FOCUS GC. Combined with a fast scanning rate, this method features excellent separation and sensitivity and generates MDLs required by the EPA method. The methods and standard operating procedure (SOP), along with a How To Manual with Quick Start Guide, can be automatically downloaded to the local PC by installing the Interactive Reference CD. A Validation Data CD may be used as a reference of typical data for the method.

EnviroLab™ Forms 2.0 software matches the workflow in environmental laboratories around the world, is simple to use, and allows novice users to be instantly productive. The DSQ II offers excellent sensitivity and reliably meets the method QC criteria. The 8260 Productivity Solution transforms the DSQ II system into a dedicated analyzer for volatiles. This allows laboratories to improve productivity and streamline new instrument integration.

For more detailed information on methods and results, please visit www. thermo.com and request Technical Note TN10210.

References

1. *US EPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Rev 3, 2006
2. 8260 Productivity Solution Standard Operation Procedure, *Determining Volatile Organics in Wastewater Using the DSQ II*. Thermo Fisher Scientific Part #120294-0001

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Application Note: 51900

Combining Hardware, Software, and Chromatography to Improve the GC/MS Analysis of Semi-Volatile Compounds

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Key Words

- ISQ Single Quadrupole GC-MS
- TRACE GC Ultra
- Semi-volatile Compounds
- US EPA Method 8270D

Introduction

Analysis of semi-volatile organic compounds by GC/MS according to well-established methodologies requires integration of a complete system of GC-MS instrumentation and software for data interpretation, analysis and reporting. While the overall process of analyzing these target compounds is a mature technique, there are continuous innovations that allow laboratories to meet lower detection limits and analyze new compounds to comply with changing regulations, with higher throughput and improved quality.

Experimental Conditions

For this experiment, a standard GC/MS method for the analysis was developed according to published quality control and method guidelines.[1] After establishing a baseline of performance according to these guidelines, improvements to the method were tested by combining changes to the chromatography, leveraging of the performance capabilities of the hardware, and applying a software package developed around routine GC/MS workflows. By combining these techniques, laboratories can increase the number of samples that can be analyzed at lower detection limits.

A Thermo Scientific ISQ GC-MS system was operated at a scan speed of 4,650 u/sec (0.1 s/scan) over a mass range of *m/z* 35 to 500 (Figure 1). The Thermo Scientific AS 3000 II autosampler was used to deliver 1 µL of sample for analysis. The Thermo Scientific TRACE GC Ultra gas chromatograph was operated in the split mode to eliminate a significant portion of the matrix. The sensitivity of the mass spectrometer was more than able to reach accepted detection limits.

Results and Discussion

Shortening Analysis Time

Many methodologies around the world accept the use of splitless injection with an analysis time of 30 minutes for a long list of active compounds. A split injection can be used if the sensitivity of the mass spectrometer is sufficient. A split injection offers several advantages, including lower detector and column maintenance, better peak shapes for volatile compounds, and increased working range with low film thicknesses which reduces column bleed rates. The method developed operates at a column flow rate of 3 mL/min and a split flow of 60 mL/min, resulting in the injection of only 5% of the sample. An example of the advantages of a split injection are shown in Figure 2.

This example shows the separation of two of the more volatile compounds – pyridine and N-nitrosodimethylamine (NDMA). Gaussian peak shapes were observed. This is due to the elimination of the adverse effects of polar solvents from the stock standard solutions. These solvent effects are more evident in a splitless injection due to the much larger amount of solvent on the column (Figure 3).

A shortened analysis time of 20 minutes was achieved using faster scan rates and a rapid oven temperature program (Figure 4). The combination of high scan speeds and fast temperature ramps results in better chromatographic separation. This is seen in Figure 5 showing separation of closely eluting analytes. Using decafluorobenzophenone (DFTPP) we are able to demonstrate expected fragmentation and resolution at these fast rates, Figure 6. The transferline design of the mass spectrometer reduces band broadening of the late eluting polynuclear aromatics (PNAs), resulting in more Gaussian peak shapes (Figure 7).

Extending the Working Range

In the analysis of waste samples, extended working ranges mean fewer dilutions and lower detection limits. The goal is to generate results from a single injection of the sample. This can only happen with a mass spectrometer with sufficient analytical linearity. A study was performed to determine the working range for the method. The instrument parameters for the study are listed in Table 1. A calibration curve was generated across the following levels: 0.5, 1, 2, 5, 10, 20, 40, 80, 160 and 200 ng/µL in methylene chloride. This is equivalent to µg/L or ppb in a standard liter sample size.

Figure 1: ISQ™ mass spectrometer and TRACE GC Ultra™ with AS 3000 II liquid autosampler

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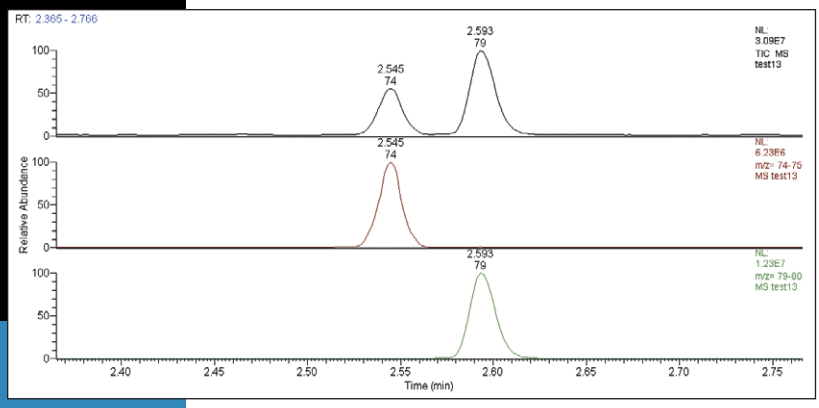

Figure 2: Gaussian peak shapes for pyridine and N-nitrosodimethylamine (NDMA) in the split mode of injection

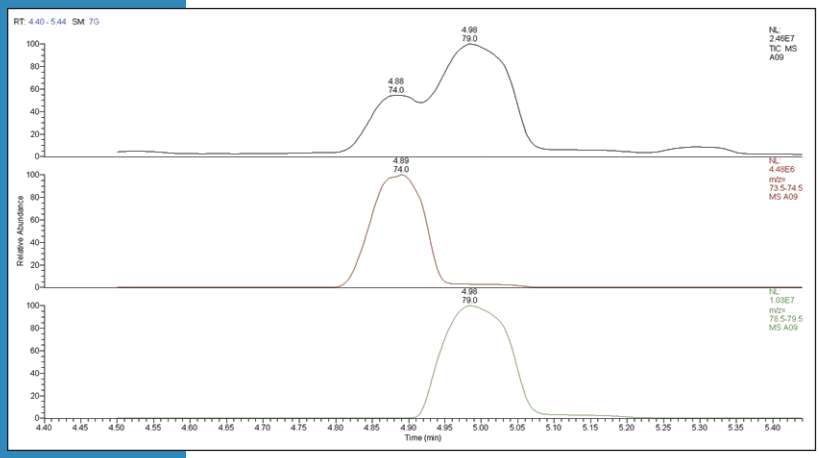

Figure 3: Distorted peaks shapes of pyridine and NDMA in the splitless mode of injection

Parameter	Conditions
Column	Trace GOLD TG-5 MS 0.25 mm × 30 meter, 0.5 µm
Inlet Liner	Siltek™ 5 mm splitless
Inlet Temperature	250 °C
Injection	Split, hot needle
Split Flow	60 mL/min
Oven Program	40 °C, 0.5 min., 14 °C/min.; 90 °C, 0 min., 22 °C/min.; 310 °C, 10 min.
Column Flow	3 mL/min
MS Transferline Temperature	310 °C
MS Source Temperature	275 °C
Multiplier Voltage	1220 V
Emmision Current	25 µA
Scan Rate	4,650 u/sec (0.1 s/scan)
Scan Range	Full Scan: *m/z* 35–500

Table 1: Instrument parameters

Once the calibration curve was acquired, the results were reviewed in Thermo Scientific EnviroLab Forms to check for any failures in the method quality control (QC) criteria. Data review is simplified in the Active View window, allowing access to all points in the calibration curve, confirming ions, and spectra for quick visual review of all compounds or only the ones that failed QC (Figure 8).

Lowering Method Detection Limits

When adequate precision is observed at lower concentrations, replicates can be made at this level that result in lower method detection limits (MDL) than are achieved with a calibration range at high levels. Eight replicate runs were made at 0.5 ng/µL in methylene chloride with the internal standards and surrogates spiked at 40 ng/µL for the determination of the instrument detection limit (IDL). The results are shown in Table 2 with an average IDL of 0.082 ng/µL.

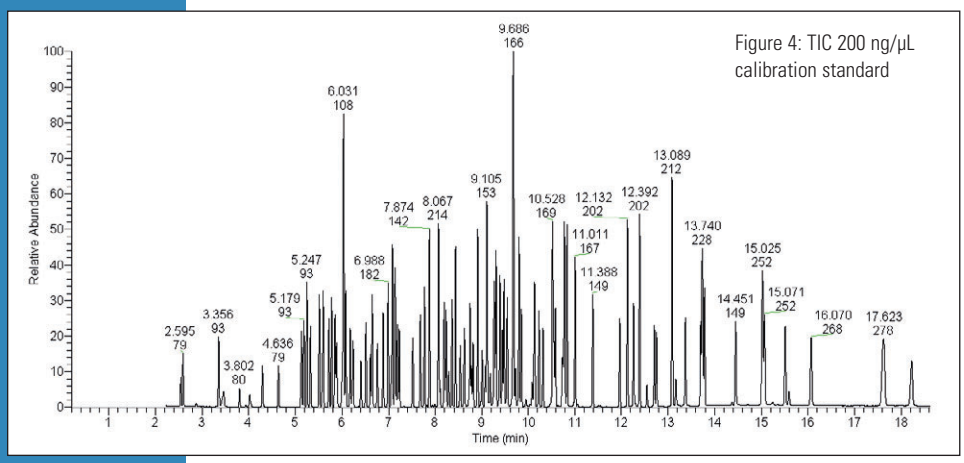

Figure 4: TIC 200 ng/µL calibration standard

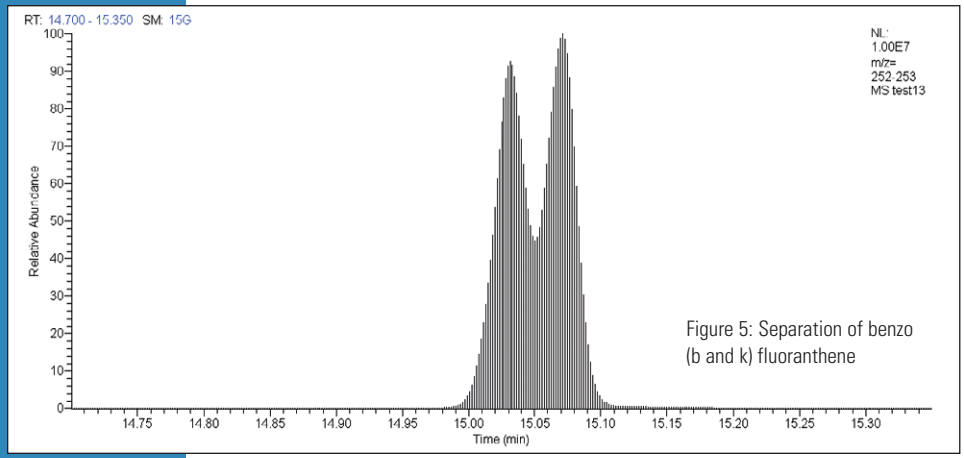

Figure 5: Separation of benzo (b and k) fluoranthene

Conclusions

After establishing a baseline of performance according to the guidelines in US EPA Method 8270D, improvements to the method were made in chromatography, taking advantage of the performance capabilities of the hardware, and applying a software package developed around routine GC-MS workflows. By combining these techniques, an average IDL of 0.023 ng/µL and an extended working range from 0.5 to 200 ng/µL was established. The improvements resulted in shorter run times and increases in overall throughput for sample analysis with less time spent in data review due to the introduction of an intelligent Active View feature in the EnviroLab Forms reporting software.

References

1. EPA Method 8270D Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Rev 4, February 2007

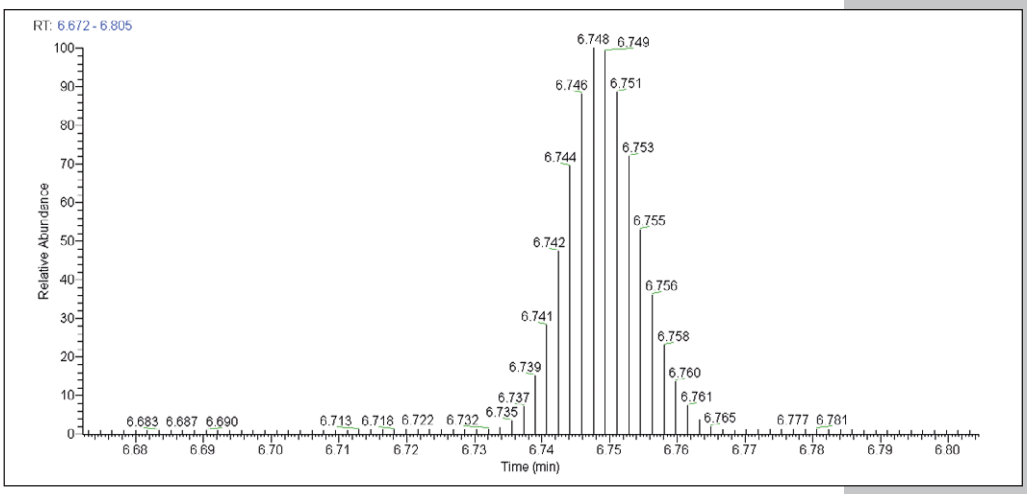

Figure 6: 20 scans across 1.8 second wide DFTPP peak, demonstrating good peak characterization

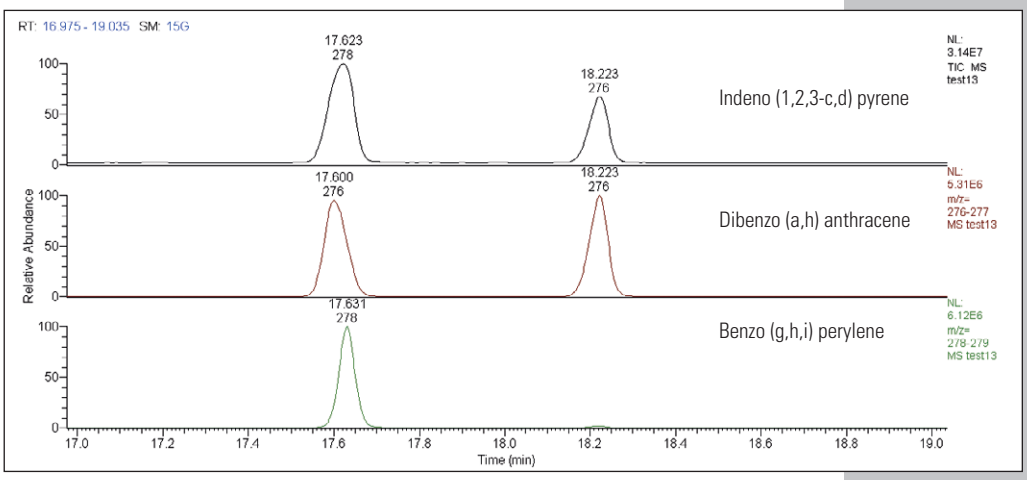

Figure 7: The transferline design of the mass spectrometer reduces band broadening of the late eluting polynuclear aromatics (PNAs): indeno (1,2,3-c,d) pyrene, dibenzo (a,h) anthracene, and benzo (g,h,i) perylene

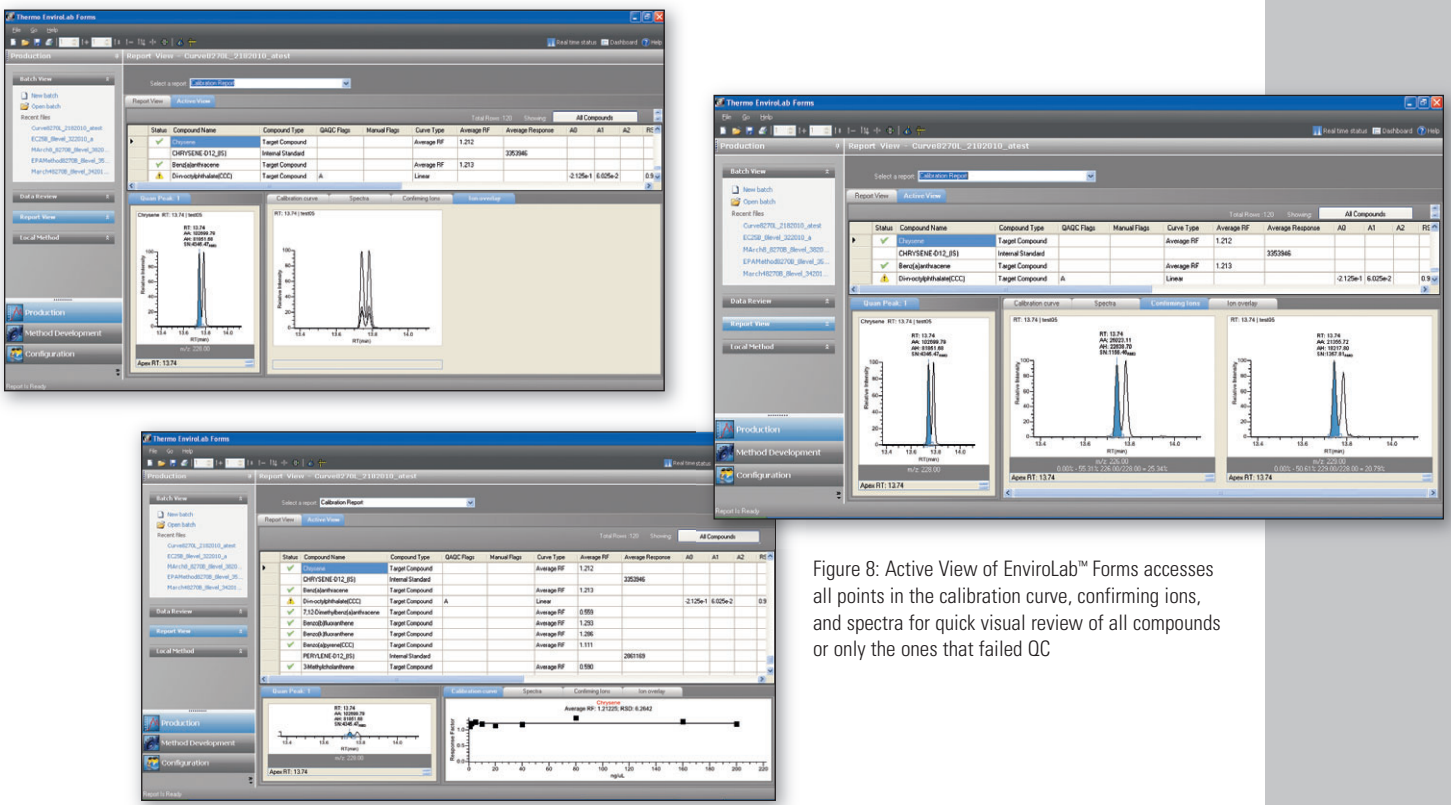

Figure 8: Active View of EnviroLab™ Forms accesses all points in the calibration curve, confirming ions, and spectra for quick visual review of all compounds or only the ones that failed QC

	% RSDs	IDL ng/µL
N-Nitrosodimethylamine	6	0.089
Pyridine RCRA	3	0.039
2-Picoline	4	0.052
N-Nitrosomethylethylamine APP9	16	0.289
Methyl methanesulfonate	9	0.171
2-fluorophenol (sur)	3	NA
N-Nitrosodiethylamine APP9	7	0.086
Ethyl methanesulfonate	8	0.092
phenol-d5 (sur)	2	NA
Phenol (CCC)	6	0.086
Aniline	5	0.072
Bis(2-chloroethyl)ether	5	0.068
Pentachloroethane	6	0.093
2-chlorophenol	5	0.068
1,3-Dichlorobenzene	4	0.054
1,4-DICHLOROBENZENE-D4 (IS)	2	NA
1,4-Dichlorobenzene (CCC)	1	0.022
Benzyl alcohol	8	0.075
1,2-Dichlorobenzene	4	0.068
2-methylphenol	10	0.126
Bis(2-chloroisopropyl)ether	4	0.055
N-Nitrosopyrrolidine APP9	6	0.075
3-Methylphenol&4-methylphenol	3	0.035
Acetophenone	6	0.084
N-Nitroso-di-N-propylamine (SPCC)	5	0.073
o-toluidine APP9	6	0.084
Hexachloroethane	7	0.101
nitrobenzene-d5 (sur)	5	NA
Nitrobenzene	5	0.084
N-Nitrosopiperidine	7	0.095
Isophorone	5	0.066
2-Nitrophenol (CCC)	7	0.072
2,4-Dimethylphenol	4	0.045
Bis(2-chloroethoxy)methane	2	0.032
2,4-Dichlorophenol (CCC)	7	0.082
1,2,4-Trichlorobenzene	5	0.074
NAPHTHALENE-D8 (IS)	4	NA
Naphthalene	4	0.056
p-Chloroaniline	7	0.078
2,6-Dichlorophenol	7	0.083
Hexachloropropene APP9	10	0.142
Hexachlorobutadiene (CCC)	6	0.099
N-Nitroso-di-N-butylamine	9	0.110
4-Chloro-3-methylphenol (CCC)	8	0.084
Safrole APP9	4	0.050
2-Methylnaphthalene	5	0.065
Hexachlorocyclopentadiene (SPCC)	4	0.045
1,2,4,5-Tetrachlorobenzene	6	0.104
2,4,5-Trichlorophenol	7	0.079
2,4,6-Trichlorophenol (CCC)	9	0.094
2-fluorobiphenyl (sur)	4	NA
Isosafrole APP9	7	0.097
2-Chloronaphthalene	5	0.077
2-Nitroaniline	9	0.096
1,4-Naphthoquinone APP9	9	0.087
Dimethyl phthalate	4	0.060
1,3-Dinitrobenzene app9	12	0.101
2,6-Dinitrotoluene	7	0.078
Acenaphthylene	3	0.044
3-Nitroaniline	15	0.115

	% RSDs	IDL ng/µL
ACENAPHTHENE-D10 (IS)	3	NA
Acenaphthene (CCC)	4	0.056
2,4-Dinitrophenol (SPCC)*	7	0.436
4-Nitrophenol (SPCC)*	6	0.545
2,4-Dinitrotoluene	7	0.073
Pentachlorobenzene	4	0.061
Dibenzofuran	4	0.061
1-Naphthylamine	5	0.068
2,3,4,6-Tetrachlorophenol	12	0.127
2-Naphthylamine	4	0.052
Diethyl Phthalate	4	0.060
4-Chlorophenyl phenyl ether	5	0.067
5-Nitro-o-toluidine APP9	9	0.080
4-Nitroaniline	18	0.105
Fluorene	3	0.039
2-Methyl-4,6-dinitrophenol*	3	0.305
Diphenylamine (CCC)	4	0.053
Azobenzene	4	0.051
2,4,6-tribromophenol (sur)	3	NA
1,3,5-Trinitrobenzene APP9	12	0.109
Diallate APP9	7	0.087
Phenacetin	15	0.080
4-Bromophenyl phenyl ether	6	0.088
Hexachlorobenzene	5	0.070
4-Aminobiphenyl	4	0.044
Pentachlorophenol (CCC)	11	0.084
Pentachloronitrobenzene	7	0.085
Pronamide	4	0.046
Dinoseb*	5	0.432
PHENANTHRENE D10 (IS)	2	NA
Phenanthrene	2	0.028
Anthracene	3	0.042
Carbazole app9	4	0.046
Di-N-butyl phthalate	5	0.058
Isodrin APP9	8	0.113
Fluoranthene (CCC)	3	0.037
Benzidine	10	0.087
Pyrene	3	0.042
p-terphenyl-d14 (sur)	2	NA
p-Dimethylaminoazobenzene	9	0.084
Chlorobenzilate APP9	7	0.073
3,3'-Dimethylbenzidine APP9	7	0.064
Butyl Benzyl Phthalate	3	0.031
Kepone APP9	23	0.196
2-Acetylaminofluorene APP9	15	0.083
3,3'-Dichlorobenzidine APP9	8	0.077
Bis(2-ethylhexyl)phthalate	8	0.071
Chrysene	3	0.050
CHRYSENE-D12 (IS)	2	NA
Benz(a)anthracene	4	0.064
Di-n-octylphthalate (CCC)	4	0.039
7,12-Dimethylbenz(a)anthracene	6	0.063
Benzo(b)fluoranthene	3	0.046
Benzo(k)fluoranthene	5	0.073
Benzo(a)pyrene (CCC)	4	0.046
PERYLENE-D12 (IS)	2	NA
3-Methylcholanthrene	7	0.071
Indeno(1,2,3-c,d)pyrene	3	0.036
Dibenzo(a,h)anthracene	4	0.055
Benzo(g,h,i)perylene	3	0.045
Average	6	0.082

**reps at 5 ng/µL*

Table 2: Instrument detection limits determined from 8 replicate injections of 0.5 ng/µL

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Thermo Scientific EnviroLab Forms 3.0 Software

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ITQ Series
Ion Trap GC-MS

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TSQ Quantum XLS
Triple Quadrupole GC-MS/MS

Environmental analysis software designed to improve your lab's efficiency

Today's environmental labs often must balance high productivity and throughput with stringent quality control protocols. The need to balance productivity with quality control protocols is critical for your lab's success. Designed for the environmental GC/MS chemist, Thermo Scientific EnviroLab Forms 3.0 software provides an integrated, workflow-oriented approach for addressing these challenges. EnviroLab™ Forms 3.0 is a user-friendly software package that provides automated processing and smart reporting for GC/MS analyses. This package is designed to complement the current full range of Thermo Scientific benchtop GC/MS systems and easily fits into the workflow of your environmental laboratory.

EnviroLab Forms adds a powerful productivity engine to the Thermo Scientific Xcalibur data system. Designed to ensure high-throughput quantitation, EnviroLab Forms is fully integrated with the stable and flexible Xcalibur™ core to provide a comprehensive system encompassing method development, data acquisition, processing, review and reporting. Both new and experienced users will find tools to automatically generate complete data set while performing sophisticated data review and reporting in an interactive manner.

EnviroLab Forms Highlights

User-Friendly

Tools and 'wizards' provide straightforward approaches for quick system loading to ensure fast generation of results.

Diverse

A wide range of reports, covering a variety of aspects of environmental work, provide documentation compliant with internal SOPs and external regulatory agencies.

Versatile

EnviroLab Forms 3.0 can be used with any of the Thermo Scientific benchtop GC/MS systems, quadrupole or ion trap. This lets your lab take full advantage of a range of acquisition modes – sequential Full Scan/SIM or Full Scan/MS^n or GC-MS/MS and H-SRM – and report these data in your required formats. Data work-up can be done at the instrument or at a separate workstation.

Automated

Once loaded, batch operations can be completely automated, generating results and reports in real-time as the sequence proceeds.

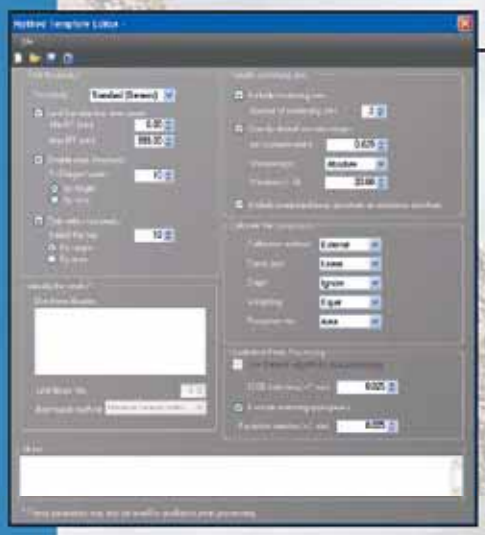
Powerful

Smart Reporting offers an integrated approach to data review and reporting. A dynamic link between these activities allows modifications to be quickly evaluated and approved.

Workflows that Fit Your Needs

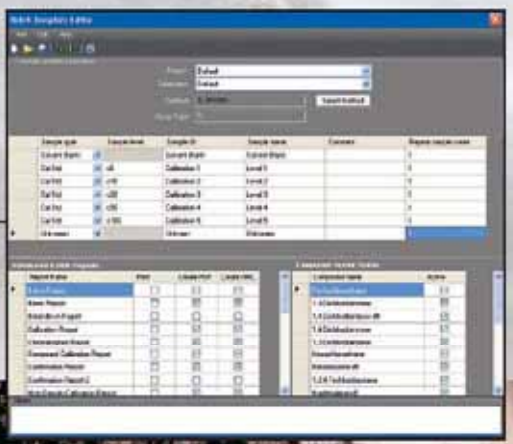
Streamline Method Development

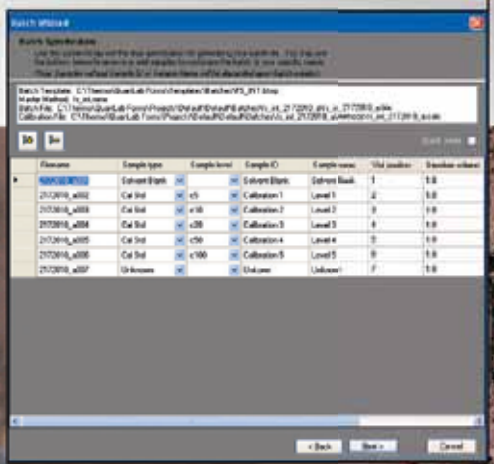
Revolutionary new "Method Forge" creates processing methods automatically from a data file. Select an acquisition method, queue the sample, and Method Forge takes care of the rest. Peaks are labeled, quantifier and qualifier ions selected, and calibration settings are generated automatically. For long compound lists, Method Forge dramatically reduces the amount of time you need to be ready to run.



Wizards and Templates Facilitate Routine Tasks

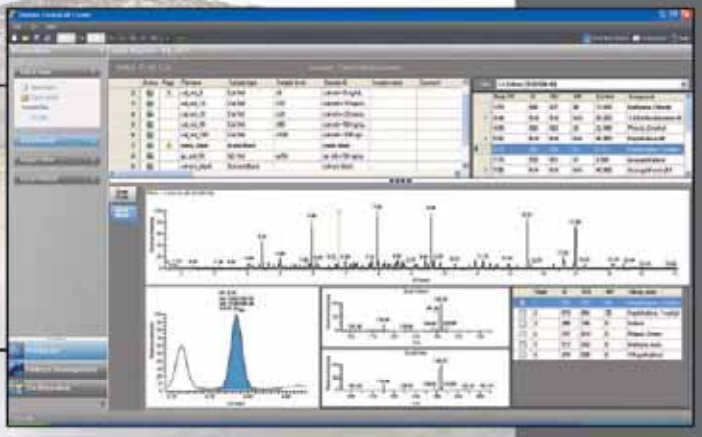
Certain tasks in your lab must be performed the same way every day. For these tasks, EnviroLab Forms offers "Wizards" and templates. Templates let you set up the framework of your batches – the items that are the same from day to day, such as matrix blanks, calibration standards, and check standards. Using the Batch Wizard, you fill in only the parts that differ from day to day – sample IDs, project details, etc. Programming time is dramatically reduced, and batches are easily referenced and stored.





Simplify Data Review and Reporting

Perhaps the most important part of quantitative analysis is reviewing batch and sample data. Data Review in EnviroLab Forms supports the analyst's critical role in this key process. Inspect sample and reference mass spectra, evaluate peak integration, review different curve fits, and observe ion ratio values – easily, and fully interactively.



Easily spot out-of-range data – correcting it can be as simple as manually changing the way the peak is integrated.

Connecting data review with data reporting revolutionizes the way you move from sample to result to report.

Smart Reporting Transforms Data Review Processes

Why is reporting data confined to a static process of putting information on a piece of paper? With EnviroLab Forms, the reporting process is an easy way to review the data. Report View in EnviroLab Forms is linked to the Data Review page. The analyst can correct a problem spot on the report to that compound and data file directly in active view without leaving the report review. In many cases, you can fix the problem, go back to the report, and the changes are reflected immediately in the reports – no reprocessing, no re-analyzing.

Product Specifications

Available Reporting Options

Flexible reporting options are available utilizing Microsoft® Excel® report templates. This allows rapid customer centric reports that are easily deployable.

Tune Report

Using a processing method to locate the peak, the tune report automatically determines a pass or fail for each ion of the specific tune compound. Pass/Fail criteria are drawn from pertinent US EPA methods.

Calibration

Report calibration curves using Average Response Factor, Linear, or Quadratic fits. The report can be generated automatically during the batch, or manually printed from Data Review. Using Smart Reporting, the Calibration Report can be selected from the active Report View. Clicking the mouse takes you back to Data Review to investigate values of interest.

Quantitation

This standard report gives the retention time, quantitation mass, area count and the calculated amount for each compound in the method, including internal standards.

Confirmation Report

This selection is generated compound-by-compound and is used to create a comprehensive report that displays the calibration curve, reference and sample spectra, and the calculated sample amount. Peak integration results for the quantitation mass and qualifying ions are displayed.

High Density Reports

For samples that may contain hundreds of target compounds, the High Density reports reduce the amount of paper used and yet still provide key results. The three report options differ in terms of the number of masses displayed per compound. The first report option simply displays the integrated quantitation mass. The second report option includes the quantitation mass and the first qualifying ion. The final high density report displays the quantitation mass and multiple qualifying ions. Each report option includes peak integration results and calculated amounts for each peak.

Tentatively Identified Compounds

Automatically generate library search information for those compounds that are not part of the quantitation processing method. A semi-quantitative amount is calculated to give estimated concentration.

Additional Reports

Batch – Print batch information on one report

Blank – Determines cleanliness of the blank, and is reported with a bounds check

Calibration Density – Report hundreds of calibration curves with the least amount of paper

Check Standard – Checks the validity of the calibration curve against a known good standard

Chromatogram – Simply report the chromatogram

Compound Calibration – A large graphical view of the calibration curve for each compound separately

Internal Standard Summary – Report all of the internal standards with bounds checking

Ion Ratio Failures – A separate report that will show which samples and compounds have ion ratio failures

LCS/LCSD – Laboratory Control Sample and the duplicate; report the complete method validity to a governing agency

Manual Integration – Report which samples were manually integrated

Method Detection Limit – A statistical determination of the detection limit of an analytical method

Method – Print the method that was used to generate the data

Method Validation – Report the deviations that are seen in the method from sample to sample

MS/MSD – Matrix spike and the duplicate; Report the efficiency of extractions for a given matrix

Surrogate Recovery – Report the extraction efficiency of compounds that are spiked into each sample that is analyzed

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Application Note: 40836

US EPA SW-846 Method 6010B using an iCAP 6500 Duo

Key Words

- ICP
- iCAP 6500
- Environmental Analysis
- SW-846 Method 6010b
- US-EPA

Introduction.

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) OF 1981 gave the US Environmental Protection Agency responsibility for cleanup of hazardous waste disposal sites. In order to assess the potential contamination and monitor cleanup of these sites, the EPA created the Contract Laboratory Program. This program directed the collection of routine environmental laboratory analytical data, to assure that quality standards were met.

Routine samples are analyzed using a fixed set of protocols with specified quality assurance and control measures.

This application note describes the performance of the Thermo Scientific iCAP 6500 Duo for EPA method 6010b. The method is suitable for the determination of 31 elements in ground waters, TCLP & EP extracts, industrial and organic wastes, soils, sludges, and sediments. All samples except filtered groundwater need to be digested prior to analysis using EPA method 3050b or similar.

Experimental

The Thermo Scientific iCAP 6000 series uses a Charged Injection Device (CID) detector, offering greater photosensitive area and lower noise for improved detection limits and better stability.

The CID detector is a non-blooming device and has the ability to measure high concentrations of matrix elements and low levels of contaminants at the same time without saturation.

Instrument conditions used for analysis are shown in Table 1 below.

Parameter	Setting	
Nebulizer	Glass Concentric	
Spray Chamber	Glass Cyclonic	
Center tube	2 mm	
Pump tubing (Tygon)	Sample Orange- White	Drain White-White
Nebulizer Gas Flow	0.7 l/min	
Plasma Gas Flow	12 l/min	
Auxiliary Gas Flow	0.5 l/min	
RF Power	1150 W	
Sample Flush Time	45 s	
Pump Speed	45 rpm	
Integration Time	Low (166 -230 nm) 15 s	High (230-847 nm) 5 s

Table 1: Instrument Parameters used for the analysis

Calibration standards were prepared in 5 % v/v HCl and 1 % v/v HNO3 at concentrations selected to cover the desired range for each element. Elements were separated as specified in 6010b to minimize interference.

Quality control solutions were run at intervals specified by the method and any necessary corrective actions were taken automatically.

The iCAP 6500 Duo allows for elements expected at low concentration to be read axially where the best sensitivity is required; the radial view was used for elements at higher concentration or for those elements that suffer from easily-ionized element interference.

An internal standard of 5 ppm scandium was automatically added on-line with the internal standard mixing kit. Details of wavelengths and plasma view for each of the analyte and internal standard elements are shown in Table 2. The analyte elements were referenced to an internal standard wavelength on the same slit and plasma view.

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Element	Wavelength	Plasma View	Internal Standard
Ag	328.068 nm	Axial	Sc 361.384 nm
Al	308.215 nm	Radial	Sc 361.384 nm
As	189.042 nm	Axial	Sc 227.318 nm
Ba	455.403 nm	Radial	Sc 361.384 nm
Be	313.107 nm	Radial	Sc 361.384 nm
Ca	315.887 nm	Radial	Sc 361.384 nm
Cd	214.438 nm	Axial	Sc 227.318 nm
Co	228.616 nm	Axial	Sc 227.318 nm
Cr	267.716 nm	Axial	Sc 361.384 nm
Cu	324.754 nm	Axial	Sc 361.384 nm
Fe	271.441 nm	Radial	Sc 361.384 nm
K	766.490 nm	Radial	Sc 631.384 nm
Mg	279.079 nm	Radial	Sc 361.384 nm
Mn	260.569 nm	Axial	Sc 361.384 nm
Na	589.592 nm	Radial	Sc 361.384 nm
Ni	231.604 nm	Axial	Sc 227.318 nm
Pb	220.353 nm	Axial	Sc 227.318 nm
Sb	206.833 nm	Axial	Sc 227.318 nm
Se	196.090 nm	Axial	Sc 227.318 nm
Tl	190.856 nm	Axial	Sc 227.318 nm
V	292.402 nm	Axial	Sc 361.384 nm
Zn	206.200 nm	Axial	Sc 227.318 nm

Table 2: Element Wavelengths

Element	Wavelength	Interfering Elements
Ag	328.068 nm	-
Al	308.215 nm	-
As	189.042 nm	Al, Fe
Ba	455.403 nm	-
Be	313.107 nm	-
Ca	315.887 nm	-
Cd	214.438 nm	Al, Fe
Co	228.616 nm	-
Cr	267.716 nm	-
Cu	324.754 nm	Fe
Fe	271.441 nm	-
K	766.490 nm	-
Mg	279.079 nm	-
Mn	260.569 nm	-
Na	589.592 nm	-
Ni	231.604 nm	-
Pb	220.353 nm	Al, Fe
Sb	206.833 nm	Al, Fe
Se	196.090 nm	Al, Fe
Tl	190.856 nm	Al, Fe
V	292.402 nm	-
Zn	206.200 nm	-

Table 3: Interelement Interferences

Significant interference from spectral overlaps can be observed due to the complex nature of the matrix for these types of samples. Major elements, such as Al, Ca, Fe, Mg, Si and P, were checked for spectral contributions on other analyte elements during method development. Once the interfering elements were identified, high-purity single element solutions were measured and the instrument software automatically calculated interference correction factors using the Interfering Element Correction (IEC) function of iTEVA software. Interferences observed are shown in Table 3.

Analysis Results

Initial Performance Checks

Method detection limits (MDL's) were established by measuring a blank solution (5 % HCl, 1 % HNO_3). The solution was analyzed seven times with each analysis having three replicates, the mean of 3x the standard deviation value from all of the runs was calculated. Results obtained are given in Table 4.

Element	Wavelength	Plasma View	MDL (ppb)
Ag	328.068 nm	Axial	0.88
Al	308.215 nm	Radial	22
As	189.042 nm	Axial	1.6
Ba	455.403 nm	Radial	0.39
Be	313.107 nm	Radial	0.29
Ca	315.887 nm	Radial	6.6
Cd	214.438 nm	Axial	0.051
Co	228.616 nm	Axial	0.26
Cr	267.716 nm	Axial	0.39
Cu	324.754 nm	Axial	0.45
Fe	271.441 nm	Radial	73
K	766.490 nm	Radial	40
Mg	279.079 nm	Radial	37
Mn	260.569 nm	Axial	0.17
Na	589.592 nm	Radial	9.3
Ni	231.604 nm	Axial	0.31
Pb	220.353 nm	Axial	0.76
Sb	206.833 nm	Axial	1.2
Se	196.090 nm	Axial	1.9
Tl	190.856 nm	Axial	0.66
V	292.402 nm	Axial	0.39
Zn	206.200 nm	Axial	0.20

Table 4: Method Detection Limits

Quality Control Procedure

Method 6010b requires that a very strict quality control procedure should be followed to ensure validity of sample data. Quality control checks are carried out following instrument calibration, during sample analysis and at the end of the analytical run. All checks must meet the required criteria for the sample data to be acceptable.

The instrument was set up using the parameters shown in Table 1 and allowed to stabilize for 30 minutes prior to calibration.

Immediately after calibration an Initial Calibration Verification (ICV) solution, calibration blank and Continuing Calibration Verification (CCV) solution were run. The calibration blank readback must be within 3 times the method detection limit for each element, while the calibration verification solutions must be within 10 % of the actual values. The standard deviation of a minimum of 2 re-samples of each verification solution must be less than 5 % for the data to be acceptable.

Analysis of the CCV solution and calibration blank was then repeated every 10 samples to ensure the instrument remained in calibration, the results for the first CCV are shown in table 5.

Element	Initial Cal Check (ICV) (mg/L)		Continuing Cal Check (CCV) (mg/L)	
	Actual	Measured	Actual	Measured
Ag	0.5	0.495	1	0.998
Al	2.5	2.553	25	25.520
As	1.0	1.019	5	5.190
Ba	0.5	0.490	5	4.862
Be	0.5	0.481	2.5	2.410
Ca	10.0	10.140	25	25.100
Cd	0.5	0.510	5	4.985
Co	0.5	0.502	5	4.909
Cr	0.5	0.46	5	4.849
Cu	0.5	0.488	5	4.951
Fe	5.0	5.060	25	24.870
K	10.0	9.935	25	25.220
Mg	6.0	6.014	25	25.120
Mn	0.5	0.494	5	4.855
Na	10.0	10.000	25	25.300
Ni	0.5	0.501	5	4.902
Pb	1.0	1.006	5	4.895
Sb	1.0	1.000	5	9.933
Se	1.0	1.008	10	10.020
Tl	1.0	1.028	10	9.566
V	0.5	0.500	5	4.909
Zn	1.0	1.020	5	4.954

Table 5: Calibration Checks

The iCAP 6000 series of spectrometers feature a highly regulated temperature control system. This temperature control ensures that the spectrum position remains constant and peak analytical performance is maintained over extended time periods even with fluctuations in the laboratory conditions.

Interference check solutions were run prior to the start of the sample analysis to verify the accuracy of the inter-element corrections factors and background correction points. Interference Check Sample A (ICSA) was prepared containing 250 mg/L each of Al, Ca, Mg and 100 mg/L Fe. Interference Check Solution AB (ICSAB) was then prepared by spiking the ICSA solution with concentrations of 0.05 to 1 mg/L for the analyte elements. The values measured for ICSAB must be within 20 % of the true value for the data to be acceptable.

Data is shown in Table 6 below.

Element mg/L	ICSA (mg/L)	ICSAB (mg/L)	Target Value (mg/L)	% Recovery
Ag	<LOD	0.212	0.210	101.0
As	0.003	0.112	0.097	115.5
Ba	0.002	0.499	0.475	105.1
Be	<LOD	0.482	0.482	100
Cd	0.001	1.052	0.916	114.8
Co	0.003	0.509	0.455	111.9
Cr	0.040	0.516	0.506	102.0
Cu	0.017	0.532	0.537	99.1
Mn	0.016	0.494	0.483	102.3
Ni	0.013	1.037	0.930	111.5
Pb	0.005	0.059	0.051	115.7
Sb	0.004	0.667	0.585	114.0
Se	0.004	0.060	0.051	117.6
Tl	0.001	0.096	0.096	100.0
V	0.005	0.500	0.481	104.0
Zn	0.045	1.060	0.975	108.7

Table 6: Interference Checks

Internal laboratory quality control checks

Method performance was verified with two different Laboratory Control Samples, a water (LCSW) and a soil digest (LCSS). The results of this are shown in table 7. The water digest was prepared by the addition of nitric acid to the sample so that the final concentration of nitric acid in the sample was 10 %. The soil digest was prepared by digesting 1 gram of sample in a mixture of nitric and hydrochloric acid and diluting the sample so the final concentration of acid was 5 % nitric acid and 1 % hydrochloric.

Element	LCSS		LCSW	
	Measured ppm	Target ppm	Measured ppm	Target ppm
Ag	0.0223	0.0209	0.479	0.495
Al	0.2722	0.3090	2.600	2.482
As	1.1750	0.9300	1.019	0.996
Ba	0.0053	[0.0053]	0.491	0.502
Be	0.0183	0.0188	0.477	0.493
Ca	175.2000	184.0005	10.410	10.180
Cd	0.0448	0.0416	0.521	0.494
Co	0.1565	0.1400	0.523	0.496
Cr	0.0982	0.0965	0.495	0.490
Cu	6.7470	6.6800	0.499	0.490
Fe	21.4300	21.0000	5.083	5.107
K	0.0579	[0.1024]	9.924	10.008
Mg	112.1000	113.0000	6.091	6.003
Mn	0.1996	0.2010	0.500	0.495
Na	0.0536	[0.0928]	10.160	10.039
Ni	0.0622	0.0568	0.518	0.492
Pb	0.2655	0.2240	1.039	0.996
Sb	0.2702	0.2130	1.006	0.992
Se	0.0473	0.0370	0.942	1.005
Tl	0.0361	0.0381	1.044	1.027
V	0.0679	0.0658	0.510	0.501
Zn	0.1751	0.1750	1.071	1.000

Table 7: Internal laboratory control checks

Conclusions

The Thermo Scientific iCAP 6500 Duo far exceeds the requirements needed to meet EPA 6010b protocols.

The instrument has a high resolution optical system which minimizes spectral interferences and reduces stray light. It uses a next generation design of the exclusive Charged Injection Device detector which offers higher sensitivity and lower noise which results in better signal to background ratios.

The integrated structural castings and precision regulated optics ensure excellent long term stability.

The results of these developments are an instrument that has extreme stability and detection limit performance which meet the requirements for this type of analysis.

References

USEPA SW-846 Method 3050b, Revision 2, December 1996.

USEPA SW-846 Method 6010b, Revision 2, December 1996.

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Application Note: 40619

US EPA SW-846 Method 6020A Using the XSERIES 2 ICP-MS

Key Words

- Environmental Analysis
- SW-846 Method 6020/6020A
- Productivity Pack
- US EPA

1. Introduction

This Application Note describes the use of the Thermo Scientific XSERIES 2 ICP-MS for SW-846 Method 6020A compliant analysis. It gives data showing compliance with each of the requirements and highlights the integrated system tools specifically designed to aid compliance. The data shown was generated using the procedures and solutions supplied in the Thermo Scientific EPA Methods Productivity Pack (Part Number 4600430). See also BR40715, *XSERIES 2 ICP-MS: EPA Methods Productivity Pack*.

2. Background

EPA History

In 1970, the United States government established the Environmental Protection Agency (EPA) in response to growing public demand for cleaner water, air and land. Prior to this, the national government was not structured to deal with pollution that caused harm to human health and degraded the environment. The EPA was tasked with repairing the damage already done and moving towards a cleaner environment. Its mission is to protect human health and to safeguard the natural environment. The Agency consists of 18,000 people in Headquarters, program offices, 10 regional offices and 17 labs across the US. The EPA provides leadership in the nation's environmental science, research, education and assessment efforts and works closely with other federal agencies and local government to develop and enforce regulations under existing environmental law. The Agency is responsible for researching and setting national standards for a variety of environmental programs and delegates the responsibility for issuing permits, and monitoring and enforcing compliance, to local government. Where national standards are not met, the EPA can issue sanctions and take other steps to assist local government in reaching the desired levels of environmental quality. The Agency also works with industries and all levels of government in a wide variety of voluntary pollution prevention programs and energy conservation efforts.

Office of Solid Waste

The EPA's Office of Solid Waste (OSW) regulates all waste under the Resource Conservation and Recovery Act (RCRA). The RCRA's goals are to:

1. Protect the public from the hazards of waste disposal
2. Conserve energy and natural resources by recycling and recovery
3. Reduce or eliminate waste, and
4. Clean up waste, which may have spilled, leaked, or been improperly disposed of.

Hazardous wastes come in many varieties. Chemical, metal, and furniture manufacturing are some examples of processes that create hazardous waste. The RCRA tightly regulates all hazardous waste from production to disposal. The RCRA also controls garbage and industrial waste. Common garbage is municipal waste, which consists mainly of paper, yard trimmings, glass, and other materials. Industrial waste is process waste that comes from a broad range of operations. Some wastes are managed by other federal agencies or state laws. Examples of such wastes are animal waste, radioactive waste, and medical waste.

The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* is the OSW's official compendium of analytical and sampling methods that have been evaluated and approved for use for analysis relating to the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements. SW-846 is a multi-volume document that changes over time as new information and data are developed. It was first issued by the EPA in 1980 and is currently in its fourth edition. Advances in analytical instrumentation and techniques are continually reviewed by the OSW and incorporated into periodic updates to SW-846 to support changes in the regulatory program and to improve method performance and cost effectiveness. To date, the EPA has finalized Updates I, II, IIA, IIB, III and IIIA of the SW-846 manual, and the updated and fully integrated manual contains approximately 3500 pages. The Methods Team of OSW has also made Draft Updates IVA and IVB available for public use.

The SW-846 volume 6020 describes the use of ICP-MS instrumentation for determining a variety of metallic elements in aqueous and solid media. In draft edition IVA, the method was replaced with 6020A.

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Methods 6020 and 6020A[1]

Both methods provide guidelines on general laboratory practices such as sample preparation, instrument setup, calibration of analytes, and interference correction equations. They also provide specific rules on various analytical practices that must be followed, including elements covered, required isotopes, quality control practices and instrument validation. Since both methods are well established and readily available in the public domain they have become widely adopted as templates for methodologies used by a host of laboratories undertaking environmental analysis world-wide. The requirements of these two important methods are broadly similar with the aim of the protocol being to ensure a consistently high quality of analytical data by enforcing compliance with a variety of stringent instrument and analytical performance checks, as outlined in Tables 1 and 2. Method 6020A extends the protocol scope to include mercury (after fixing all analytical solutions with 2 mg/L gold) and contains an alteration on interference checking in that the concentration of interferent species is increased in the interference check solutions.

[1]Note that Method 6020A, along with all Draft Update IVA SW-846 methods, may be downloaded from the EPA OSW website: http://www.epa.gov/SW-846/up4a.htm#6_series. Update III methods, including 6020, may be downloaded from the following webpage: http://www.epa.gov/epaoswer/hazwaste/test/6_series.htm.

CHECK CODE	CHECK NAME	PURPOSE	FREQUENCY	LIMITS
-	Mass Calibration/ resolution setting	ensures the correct mass is measured at its maximum and that peaks are properly resolved	prior to each analytical run (daily)	masses measured must not deviate by more than 0.1 amu from their nominal position and peak width must be <0.9amu at 10 % peak height
-	Stability and precision	ensures the instrument is properly optimised and thermally stable	prior to each analytical run (daily)	<5 % RSD on at least 4 measurements
-	Calibration	calibrates the instrument response for measurement	daily or when required	-
IDL	Instrument detection limit	estimates the detection limit of the instrument from 7 analyses of a blank over 3 non-consecutive days	every 3 months or after major instrument maintenance or hardware replacement	-

Table 1 - Summary of Instrument Calibration and Check Requirements

QC CODE	QC NAME	PURPOSE	FREQUENCY	LIMITS
ICV	Initial Calibration Verification	checks the calibration against a second calibration source	After initial calibration	90-110 %
ICB	Initial Calibration Blank	initial check of read-back at blank level	After initial calibration	<3* IDL
ICSA	Interference Check Solution A	checks for freedom from interference	After initial calibration	No specific requirements
ICSAB	Interference Check Solution AB	checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	No specific requirements

Table 2 - Summary of Quality Control Requirements

QC CODE	QC NAME	PURPOSE	FREQUENCY	LIMITS
CCV	Continuing Calibration Verification	a continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110 %
CCB	Continuing Calibration Blank	a continuing periodic check on the read-back at blank levels	After each calibration and every 10 samples	<3* IDL
PDS	Post Digestion Spike	checks the recovery of analytes spiked into an unknown sample after preparation (digestion)	1 per 20 samples per matrix	75-125 %
DUP	Duplicate	checks the reproducibility of results by analysing an unknown sample in duplicate	1 per 20 samples per matrix	±20% RPD
SER	Serial Dilution	checks for matrix effects by assessing the variation of results for an unknown sample before & after dilution	1 per 20 samples per matrix	±10 % of the original undiluted result after dilution correction
LCS	Laboratory Control Sample	checks the accuracy of the entire analytical process	Every 20 samples	80-120 %

Table 2 - Summary of Quality Control Requirements (continued)

3. Experimental

3.1 Equipment

An XSERIES 2 ICP-MS (Thermo Fisher Scientific, Bremen, Germany) was setup in the standard configuration, using an ASX-510 autosampler (Cetac, Omaha, Nebraska, USA). Internal standard was added on-line, using a Y-piece (On-line Internal Standard Addition Kit P/N 4600431). The instrument was optimized using the autotune function when required. The instrument parameters are given in Table 3.

PARAMETER	VALUE
RF Power (W)	1400
Cool Gas Flow (L/min)	13
Auxiliary Gas Flow (L/min)	0.8
Nebuliser Gas Flow (L/min)	0.85-0.90
Sample Uptake Rate (mL/min)	0.4 approx.
Sample Introduction System	Concentric nebulizer with low-volume impact bead spraychamber (not cooled) and one-piece torch (1.5mm ID injector)
Cones	Nickel, Xi Design
Detector	Simultaneous pulse/analogue
Uptake Time	25 seconds at 50 rpm
Stabilization Delay	10 seconds at 17 rpm
Wash Time	40 seconds at 50 rpm
Survey Runs	1 - scanning
Main Runs	3 - peak jumping
-Number of Points per Peak	1
-Dwell Time / Point	5 - 50 ms
-Number of Sweeps / Replicate	25
Internal Standardization Technique	Interpolation, using ^{6}Li, ^{45}Sc, ^{115}In, ^{159}Tb
Total Time per Sample	2:45 minutes

Table 3 - XSERIES 2 Parameters

3.2 Calibration Solutions

High purity reagents were used throughout. Ultra pure water of resistivity >18 M cm (Milli-Q) was used, along with super purity grade nitric and hydrochloric acids (Romil, Cambridge, UK). All analytical solutions were prepared from ICP-MS grade stock standards from the EPA Productivity Pack solutions (Thermo Scientific P/N 4600430) and reference samples (NIST, Gaithersburg, MD, USA) were analysed along with known and unknown samples courtesy of the Environment Agency, UK. Table 4 gives the calibration concentrations.

STANDARD	CONCENTRATION
Low Concentration Elements - Standard 1	250 µg/L Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb
Low Concentration Elements - Standard 2	500 µg/L Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb
High Concentration Elements - Standard 1	50 mg/L Na, Mg, K, Ca, Fe
High Concentration Elements - Standard 2	100 mg/L Na, Mg, K, Ca, Fe

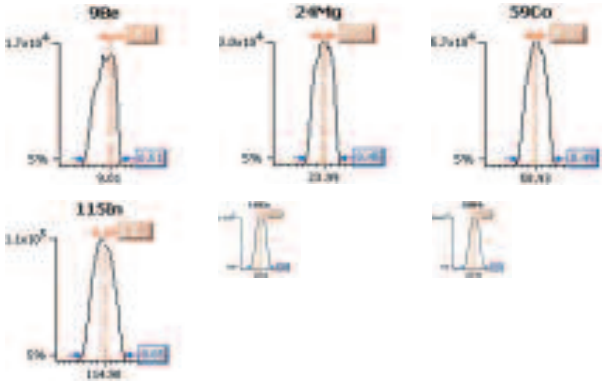
Table 4 - Calibration Standards - Concentrations

3.3 Instrument Checks

To ensure that the mass-calibration, resolution and stability requirements are met, the XSERIES 2 has critical hardware and PlasmaLab software features built-in. The hardware has two variable resolution modes allowing high and standard resolution settings to be defined. Standard resolution is typically set to give peaks of approximately 0.75 amu width at 5 % peak height, whilst high resolution is typically set to give around 0.4 amu. Normally the excellent abundance sensitivity specification of the XSERIES 2 quadrupole will allow low concentration analytes to be measured next to very large interferences at peak width settings of 0.75amu. However, these settings may be adjusted within the software to ensure no peak-tailing from high concentration species affects measurement of adjacent-mass low concentration analytes. PlasmaLab allows the instrument to be mass-calibrated whenever required. The mass calibration, the peak widths, and the precision over five measurements may be checked using a *Performance Report*. The *Performance Report* is a user definable test that may be run as part of an analytical method or separately as a setup function. Figures 1 and 2 show data from a Performance Report in the format in which it is generated.

Performance Report

Mass Calibration verification



Analyte	Limits			Results	
	Max. width	Min. width	Max. error	Peak width	Peak error
9Be	0.75	0.40	0.10	0.51	0.03
24Mg	0.75	0.40	0.10	0.45	-0.03
59Co	0.75	0.40	0.10	0.49	-0.01
115In	0.75	0.40	0.10	0.65	-0.05
140Ce	0.75	0.40	0.10	0.65	-0.03
208Pb	0.75	0.40	0.10	0.71	0.01

Figure 1 - Performance Report Results for Mass Calibration and Resolution Checks

Sample details

Acquired at : 12/12/2002 14:08:12
Report name : EPA ILM05.2 / 6020A 2.1 [12/12/2002 13:56:01]

Sensitivity and stability results
Acquisition parameters

Sweeps : 180

run	time	5Bkg	9Be	24Mg	59Co	115In	140Ce	156Ceo	208Pb	220Bkg
Dwell (mSecs)		100.0	10.0	10.0	10.0	10.0	10.0	30.0	10.0	100.0
Limits	% RSD	-	2.0 %	2.0 %	2.0 %	2.0 %	2.0 %	-	2.0 %	-
	Countrate	<2	>5000	>5000	>10000	>50000	>10000	-	>25000	<2
1	14:08:24	0.000	16797	33832	61243	112879	116767	1962	100691	0.222
2	14:09:23	0.000	16640	33338	61235	113079	116573	1935	100713	0.111
3	14:10:23	0.000	16894	33514	61133	113174	117136	1964	100805	0.444
4	14:11:23	0.167	17027	33294	61436	112328	117146	1948	100657	0.000
5	14:12:23	0.056	16536	33001	61020	112235	116563	1998	100517	0.056
x		0.044	16779	33396	61214	112739	116837	1961	100677	0.167
SD		0.07	195	305	153	432	289	23	104	0.18
% RSD		162.980	1.168	0.916	0.252	0.383	0.248	1.209	0.104	105.409

Ratio results

RUN	TIME	156Ce O/140Ce
	Ratio limits	< 0.0200
1	14:08:24	0.017
2	14:09:23	0.017
3	14:10:23	0.017
4	14:11:23	0.017
5	14:12:23	0.017
x		0.0168
SD		0.00
% RSD		1.2931

Result : The performance report passed.

Figure 2 - Performance Report Results for Sensitivity and Stability Checks

3.4 Method Development

Prior to running real samples, 6020A requires that several checks are performed. This section outlines the method requirements and details proof work to validate the instrument.

Interference Study

Appropriate interference corrections must be implemented and although the EPA methods suggest many theoretical correction equations including factors, they recommend that the actual factors used should be empirically determined for each individual instrument.

An interference correction strategy was formulated and assessed on a standard XSERIES 2 instrument by running high purity single element calibrations reflecting likely environmental sample matrix components. Potential interferents studied include Ca, Na, Fe, Al, Mg, Ti, Mo, P, K, S, C, and Cl. Interferences were observed by inspecting the countrates for analyte species as a function of increasing concentration of the interferent species. Appropriate ratios were used to calculate correction factors where necessary. Table 5 gives the interference correction equations used during the XSERIES 2 analytical performance assessment. Note that these correction factors were derived during several days of tests on two different instruments. The same set of factors were used for all subsequent analysis on two instruments after the evaluation, showing that the interference corrections are extremely stable and accurate from day to day, even with different instruments.

PARAMETER	VALUE
Analyte	Correction Equation
51V	= 51M - 3.0460 * 53Cl O
53Cl O	= 53M - 0.1140 * 52Cr
52Cr	= 52M - 0.0050 * 13C
56Fe	= 56M - 0.1500 * 43Ca
60Ni	= 60M - 0.0020 * 43Ca
75As	= 75M - 2.9000 * 77ArCl
77ArCl	= 77M - 0.8000 * 82Se
82Se	= 82M - 1.0010 * 83Kr
108MoO	= 1805M - 0.7120 * 106Cd
111Cd	= 111M - 0.9820 * 108MoO
114Cd	= 114M - 0.0270 * 118Sn
115In	= 115M - 0.0140 * 118Sn
123Sb	= 123M - 0.1240 * 125Te
208Pb	= 208M + 1.0000 * 206Pb + 1.0000 * 207Pb

Table 5 - Interference Correction Equations

Linear Dynamic Range (LDR)

The LDR for the XSERIES 2 instrument was assessed in the analytical configuration used for analysis by measuring standards of increasing decades of concentration, from 1 µg/L - 10 mg/L (50 µg/L - 500 mg/L for Na, Mg, K, Ca, Fe). Table 6 gives the linear range found for the XSERIES 2.

ANALYTE	LINEAR RANGE (mg/L)
Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Sb, Ba, Tl, Pb	10
Na, Mg, K, Ca, Fe	500

Table 6 - Linear Ranges

Instrument Detection Limit (IDL)

The 6020A document specifies that IDLs must be determined every three months for each instrument. There are no specific requirements, but the IDLs form the basis of subsequent QC blank checking

6020A describes a protocol for determining the MDL as follows. The instrument hardware and method must be set up as intended for sample analysis. The instrument detection limit (IDL) is estimated from the mean standard deviation of a multiple replicate blank analysis, in concentration units. Seven repeats are required over three non-consecutive days. The data for IDL calculation must have all the required calculations included, e.g. interference correction equations as these can have a substantial influence on the IDL. Table 7 lists IDL values obtained. The ICP-MS systems these data were obtained from were instruments in regular use in an open laboratory environment. The hardware components were exposed to a wide range of sample types, i.e. the cones, spraychamber and sample introduction system were conditioned with environmental matrices before data collection. These method detection limits represent achievable data using a basic XSERIES 2 instrument in a standard laboratory environment using ultra pure water and super pure acids.

IDLS (3 BATCHES OF 7 FULL ANALYSES)

ELEMENT	UNITS	1% HNO3	2 % HCL
9Be	µg/L	0.006	0.01
23Na	mg/L	0.0006	0.003
25Mg	mg/L	0.00003	0.0003
27Al	µg/L	0.03	0.2
39K	mg/L	0.002	0.01
44Ca	mg/L	0.001	0.006
51V	µg/L	0.01	0.3
52Cr	µg/L	0.01	0.1
55Mn	µg/L	0.003	0.02
56Fe	mg/L	0.0006	0.001
59Co	µg/L	0.001	0.002
60Ni	µg/L	0.01	0.02
65Cu	µg/L	0.006	0.01
66Zn	µg/L	0.01	0.03
75As	µg/L	0.03	0.2
77Se	µg/L	0.06	2
78Se	µg/L	0.2	1
82Se	µg/L	0.1	0.1
107Ag	µg/L	0.06	0.6
111Cd	µg/L	0.02	0.1
114Cd	µg/L	0.001	0.002
121Sb	µg/L	0.001	0.02
137Ba	µg/L	0.006	0.006
205Tl	µg/L	0.001	0.002
208Pb	µg/L	0.001	0.003

Table 7 - IDLs in 1 % HNO3 and 2 % HCl

3.5 Performance Evaluation

The performance of an XSERIES 2 was evaluated by running the quality control system required for 6020A. Data were acquired over three non-consecutive days, at

the same time as acquiring the IDL data. Samples representing a variety of matrices, including tap water, river water, industrial effluent, digestates of soil, sediment and biota (liver tissue), were analysed. Each sample was subjected to the QC requirements of 6020A, i.e. analysed in duplicate, after serial dilution and after spike addition.

The sample list was as follows:

SAMPLE NAME	SAMPLE TYPE	PURPOSE
Instrument Cal and cross-cal	Instrument Setup	Mass calibration, detector voltage set-up
Tune	Instrument Setup	Performance report and Autotune if required
Blank	Blank	
LoCal1	Fully Quant Standard	
LoCal2	Fully Quant Standard	Calibration
HiCal1	Fully Quant Standard	
HiCal2	Fully Quant Standard	
ICV	QC Sample	Calibration accuracy check with 2nd source standard
ICB	QC Sample	Initial blank check
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check
LCS	QC Sample	Accuracy check with NIST 1640 River Water
ISCA 6020A	QC Sample	Blank check in the presence of interferences
ICSAB 6020A	QC Sample	Recovery check in the presence of interferences
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check
Sample 1	Unknown	Unknown sample 1
Sample 1 DUP	QC Sample	Unknown sample 1 repeated
Sample 1 SER	QC Sample	Unknown sample 1 diluted 1+4 with 1 % nitric acid
Sample 1 SPK	QC Sample	Unknown sample 1 spiked
Sample 2	Unknown	Unknown sample 2
TO		
Sample n	Unknown	Unknown sample n
CCV	QC Sample	Calibration accuracy/drift check
CCB	QC Sample	Blank check

4. Results and Discussion

4.1 Initial Calibration Verification (ICV)

The ICV sample is a solution prepared from an alternative source of starting materials to those of the calibration. Its purpose is to check the accuracy immediately after calibration. The ICV was set at 40 % of the top standard in this case. The measured concentrations must be within 10 % of the known values. Table 8 gives the results of ICV measurements from 36 determinations over three non-consecutive days.

ANALYTE	UNITS	MEAN (N=36)	KNOWN	% REC
9Be	µg/L	191	200	96
23Na	mg/L	40	40	100
25Mg	mg/L	40	40	101
27Al	µg/L	198	200	99
39K	mg/L	40	40	100
44Ca	mg/L	40	40	100
51V	µg/L	201	200	101
52Cr	µg/L	198	200	99
55Mn	µg/L	196	200	98
56Fe	mg/L	40	40	101
59Co	µg/L	196	200	98
60Ni	µg/L	191	200	95
65Cu	µg/L	187	200	94
66Zn	µg/L	186	200	93
75As	µg/L	205	200	102
77Se	µg/L	956	1000	96
78Se	µg/L	957	1000	96
82Se	µg/L	959	1000	96
107Ag	µg/L	183	200	91
111Cd	µg/L	192	200	96
114Cd	µg/L	190	200	95
121Sb	µg/L	191	200	96
137Ba	µg/L	201	200	100
205Tl	µg/L	195	200	98
208Pb	µg/L	190	200	95

Table 8 - ICV Results

The results in Table 8 show that the calibration was consistent with the second source stock used for the ICV. The results (91-102 %) are within the required limits of 90-110 %. The result for Ag is slightly low at 91 %, although there are well known stability problems with this element due to precipitation as AgCl in the presence of chloride.

4.2 Continuing Calibration Verification (CCV)

The CCV sample is designed to continuously check accuracy by periodic analyses interspersed between analyses of unknowns. The CCV was set at 60 % of the top standard in this case. Again, the measured concentrations must be within 10 % of the known values. Table 9 gives the results of CCV measurements from 99 determinations over three non-consecutive days.

ANALYTE	UNITS	MEAN (N=99)	KNOWN	%REC
9Be	µg/L	284	300	95
23Na	mg/L	61	60	102
25Mg	mg/L	61	60	102
27Al	µg/L	310	300	103
39K	mg/L	62	60	103
44Ca	mg/L	62	60	103
51V	µg/L	304	300	101
52Cr	µg/L	299	300	100
55Mn	µg/	304	300	101
56Fe	mg/L	62	60	103
59Co	µg/L	299	300	100

Table 9 - CCV Results.

ANALYTE	UNITS	MEAN (N=99)	KNOWN	% REC
60Ni	µg/L	289	300	96
65Cu	µg/L	284	300	95
66Zn	µg/L	280	300	93
75As	µg/L	295	300	98
77Se	µg/L	282	300	94
78Se	µg/L	284	300	95
82Se	µg/L	282	300	94
107Ag	µg/L	289	300	96
111Cd	µg/L	287	300	96
114Cd	µg/L	285	300	95
121Sb	µg/L	293	300	98
137Ba	µg/L	304	300	101
205Tl	µg/L	297	300	99
208Pb	µg/L	293	300	98

Table 9 - CCV Results (continued)

The results given in Table 9 show that the instrument consistently gives accurate results, even after running the ICS solutions and real samples. The determined range (93-103 %) is well within the required range of 90-110 %.

4.3 Laboratory Control Sample (LCS)

In this case the River Water reference material, NIST 1640, was analyzed as a LCS. The results from 36 determinations over 3 non-consecutive days are summarized in Table 10. These must lie within 10 % of the known value.

ANALYTE	UNITS	MEAN (N=36)	REF VALUE	% REC
9Be	µg/L	36.58	34.94	105
23Na	mg/L	30.39	29.35	104
25Mg	mg/L	6.14	5.819	106
27Al	µg/L	52.23	52	100
39K	mg/L	0.98	0.994	99
44Ca	mg/L	7.15	7.045	101
51V	µg/L	12.86	12.99	99
52Cr	µg/L	37.73	38.6	98
55Mn	µg/L	122.5	121.5	101
59Co	µg/L	20.79	20.28	102
60Ni	µg/L	27.66	27.4	101
65Cu	µg/L	85.28	85.2	100
66Zn	µg/L	53.19	53.2	100
75As	µg/L	27.34	26.67	103
82Se	µg/L	22.82	21.96	104
111Cd	µg/L	23.26	22.79	102
114Cd	µg/L	22.93	22.79	101
121Sb	µg/L	13.42	13.79	97
137Ba	µg/L	149.9	148	101
208Pb	µg/L	27.06	27.89	97

Table 10 - LCS Results

The results given in Table 10 show that the instrument consistently produces accurate data for real environmental samples, such as the NIST River Water reference material, 1640. All measured values (97-106 %) are well within the allowable range of 90-110 %.

4.4 Interference Check Solutions (ICSA & ICSAB)

Solution ICSA is analysed to check the effect of interference on the results at blank levels, whilst ICSAB checks the recovery of analytes in the presence of interference. Both solutions contain the following interferent species: 2000 mg/L chloride, 300 mg/L Ca, 250 mg/L Na, Fe, 200 mg/L carbon, 100 mg/L Al, Mg, P, S, K, and 2 mg/L Mo, Ti. ICSAB additionally contains the following analytes: 50 µg/L Ag, 100 µg/L As, Cd, Se, Zn, 200µg/L Co, Cr, Cu, Mn, Ni, V. There are no specific requirements for the results of the interference checks. Table 11 gives the results for the ICS solutions.

		ICSA			ICSAB		
ANALYTE	UNITS	MEAN (N=30)	KNOWN	%REC	MEAN (N=30)	KNOWN	% REC
6Li	%	*71.74*			*70.94*		
9Be	µg/L	0.12			0.091		
23Na	mg/L	240	250	96	242	250	97
25Mg	mg/L	102	100	102	103	100	103
27Al	µg/L	100115	100000	100	100819	100000	101
39K	mg/L	104	100	104	105	100	105
44Ca	mg/L	318	300	106	323	300	108
45Sc	%	*70.87*			*70.71*		
51V	µg/L	2.0			205	200	103
52Cr	µg/L	0.90			199	200	99
55Mn	µg/L	2.9			199	200	99
56Fe	mg/L	253	250	101	255	250	102
59Co	µg/L	0.73			191	200	96
60Ni	µg/L	-1.14			175	200	88
65Cu	µg/L	1.9			169	200	84
66Zn	µg/L	13			89	100	89
75As	µg/L	0.49			91	100	91
77Se	µg/L	4.7			85	100	85
78Se	µg/L	4.6			86	100	86
82Se	µg/L	-0.30			80	100	80
107Ag	µg/L	1.9			32	50	64
111Cd	µg/L	0.33			87	100	87
114Cd	µg/L	1.14			87	100	87
115In	%	*74.00*			*73.71*		
121Sb	µg/L	0.66			0.58		
137Ba	µg/L	2.6			2.4		
159Tb	%	*77.80*			*78.51*		
205Tl	µg/L	0.033			0.025		
208Pb	µg/L	1.9			1.9		

Table 11 - ICS Solution Results

The results given in Table 11 show that accurate results are consistently achieved for the high concentration elements such as Mg, Al, K at the 100 mg/L level, Ca at the 300 mg/L, and Fe and Na at the 250 mg/L level. Accurate data were even achieved for Al at 100 mg/L after calibration for this analyte to only 0.5 mg/L. This demonstrates the excellent linear range of the instrument. The results of ICSA show that the presence of interferences do not contribute dramatically to the analyte signals at the blank level, with the majority of results in the single figure µg/L range or lower. This indicates that, where used, the interference correction equations work well, e.g. the case of As in the presence of chloride (ArCl interference) or Ni in the presence of Ca (CaO interference). Furthermore, where not used, the interference contributions are still extremely low due to the characteristics of the Xi interface, e.g. 77Se in the presence of chloride (ArCl

interference). Two exceptions to the generally excellent ICSA results are Zn and Mn, which are slightly high due to the presence of contamination. The Mn contamination was confirmed by acquiring a mass spectrum in standard resolution mode for an independently prepared 250 mg/L Fe solution and a 50 ng/L Mn standard (Figure 4). This shows that even in the presence of 250 mg/L Fe, the mass 56 signal for Fe does not contribute to the Mn signal at mass 55.

The results of ICSAB show that accurate data may be achieved at the µg/L level in the presence of interferences, with the exception of Ag. The low Ag value is due to the precipitation of AgCl as the solution contains 2000 mg/L of chloride. The internal standard percentages show that the presence of high matrix levels do not produce excessive signal suppression, with the worst case being Li with approximately 30 % signal loss.

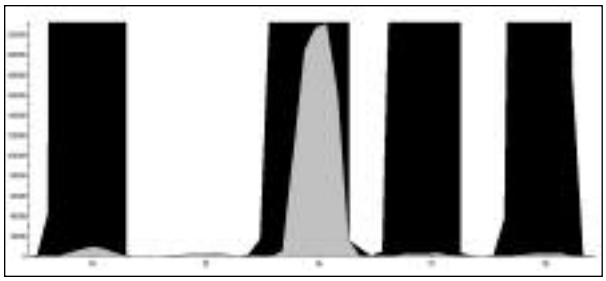


Figure 4 - Spectrum for 250 mg/L Fe (black) and 500 ng/L Mn (grey)

4.5 Sample AQC

The method requires that once every 20 samples per matrix, a sample must be analyzed in duplicate (DUP), after a 1+4 serial dilution (SER) and after the addition of a post digestion spike (PDS). The Relative Percentage Difference (RPD) is calculated for each duplicate and serial dilution (relative to the original sample) - see Equation 1. This test is not applied if either of the results is less than 50*IDL. The PlasmaLab software is able to automatically disqualify results from having this test applied due to the result being less than 50*IDL. Similarly, a spike recovery test will not be applied if the sample result is greater than a user definable percentage of the spiked concentration.

Equation 1 - Calculation of % RPD for Duplicates

$$\% RPD = 100 * (i - d) / \{(i + d) / 2\}$$

where i is the initial sample result, and d is the duplicate result

Equation 2 - Calculation of % RPD for Serial Dilutions

$$\% RPD = 100 * (i - s) / i$$

where i is the initial sample result, and s is the dilution corrected serial dilution result

Equation 3 - Calculation of % Spike Recovery

$$\% REC = 100 * (a - i) / k$$

where i is the initial, unspiked sample result, a is the sample result after spike addition, and k is the known spike concentration

The method requires that the RPD values are less than 20 %, while the spike recoveries are within 25 % of the known addition value. Tables 12-16 give the results and AQC results for a variety of sample types treated in this way. Tables 14 gives the results for multiple analyses of a sediment reference material digested using an aqua regia digestion.

		TAP WATER (N=9)				
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	µg/L	0.02			50	118
23Na	mg/L	10.9	0.55	0.64		
25Mg	mg/L	3.86	0.83	0.31		
27Al	µg/L	11.9			2000	89
39K	mg/L	1.63	1.3	2		
44Ca	mg/L	31.9	0.5	4.9		
51V	µg/L	0.278			500	100
52Cr	µg/L	0.147			200	98
55Mn	µg/L	1.92			500	99
56Fe	mg/L	0.05				
59Co	µg/L	0.11			500	99
60Ni	µg/L	2.30			500	98
65Cu	µg/L	199	0.57	0.37	250	98
66Zn	µg/L	189	0.78	3.4	500	97
75As	µg/L	4.82			40	100
82Se	µg/L	0.53			10	93
107Ag	µg/L	0.415				
111Cd	µg/L	0.067			50	98
114Cd	µg/L	0.097			50	97
121Sb	µg/L	0.122			100	93
137Ba	µg/L	89.4			2000	105
205Tl	µg/L	0.005				
208Pb	µg/L	9.82			20	94

Table 12 - Tap Water Results

Very few analytes in the tap water were above 50*IDL and therefore few duplicate or serial dilution tests could be applied. Those that are, show relative percentage differences (RPDs) that were well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride.

		EFFLUENT (N=9)				
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	µg/L	14.2	5.0	3.9	50	96
23Na	mg/L	23.2	2.2	1.5		
25Mg	mg/L	12.4	0.9	4.9		
27Al	µg/L	440	2.4	1.2	2000	93
39K	mg/L	4.15	1.9	1.9		
44Ca	mg/L	77.1	2.2	0.5		
51V	µg/L	60.7	3.1	3.0	500	96
52Cr	µg/L	32.5	3.4	3.6	200	94
55Mn	µg/L	75.5	4.0	1.7	500	94
56Fe	mg/L	1.81	2.5	5.0		
59Co	µg/L	58.6	2.6	3.3	500	92
60Ni	µg/L	57.7	3.0	4.3	500	91
65Cu	µg/L	82.8	2.8	5.2	250	91
66Zn	µg/L	67.2	4.5	2.8	500	91

Table 13 - Effluent Results

EFFLUENT (N=9)						
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
75As	µg/L	38.6	1.8	1.2	40	93
82Se	µg/L	21.2	1.4	2.3	10	95
107Ag	µg/L	2.72				
111Cd	µg/L	14.6	0.3	3.7	50	93
114Cd	µg/L	14.5	1.9	5.6	50	93
121Sb	µg/L	18.6	2.5	0.3	100	93
137Ba	µg/L	456	1.4	4.7	2000	102
205Tl	µg/L	12.5	1.1	3.9		
208Pb	µg/L	12.3	1.4	4.4	20	96

Table 13 - Effluent Results (continued)

Most analytes in the effluent were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride.

CLYDE SEDIMENT REFERENCE MATERIAL 1 (N=9)								
ANALYTE	UNITS	SAMPLE RESULT	KNOWN (mg/kg)	%REC	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	1.95			0.4		50	98
23Na	mg/kg	5030	4515	111	1.5	1.7		
25Mg	mg/kg	5480	4667	117	0.5	5.1		
27Al	mg/kg	33575	24975	134	0.3	2.5	2000	121
39K	mg/kg	2070	1982	104	1.0	4.4		
44Ca	mg/kg	4120	3455	119	0.0	9.3		
51V	mg/kg	32.5	30.9	105	0.9	6.9	500	102
52Cr	mg/kg	157	153	102	0.9	4.5	200	100
55Mn	mg/kg	385	364	106	1.6	4.9	500	102
56Fe	mg/kg	25100	23786	106	1.9	5.1		
59Co	mg/kg	10.2	10.5	97	0.2	5.1	500	102
60Ni	mg/kg	27.7	28	99	0.3	6.1	500	98
65Cu	mg/kg	97.0	96	101	0.8	6.9	250	97
66Zn	mg/kg	294	290	101	0.7	6.2	500	98
75As	mg/kg	10.6	11.1	96	2.5	6.6	40	99
82Se	mg/kg	1.27					10	97
107Ag	mg/kg	5.51						
111Cd	mg/kg	1.18	1.045	113	4.6	1.3	50	99
114Cd	mg/kg	1.04	1.045	100	0.9	5.4	50	100
121Sb	mg/kg	0.516					100	95
137Ba	mg/kg	264					2000	107
205Tl	mg/kg	0.255						
208Pb	mg/kg	125	123	101	1.4	1.0	20	100

Table 14 - Sediment Results

Most analytes in the Clyde Sediment Digest were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction. The measured values agree extremely well with the reference values, all being within 20 % of the known value, with the exception of Al which is slightly high, possibly due to contamination.

STONY SOIL DIGEST (N=9)						
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	3.28	9.4	4.6	50	99
23Na	mg/kg	775	0.2	4.5		
25Mg	mg/kg	11060	2.7	5.7		
27Al	mg/kg	25843	0.6	2.7	2000	95
39K	mg/kg	12690	1.0	2.1		
44Ca	mg/kg	32400	0.8	2.7		
51V	mg/kg	476	0.3	2.3	500	98
52Cr	mg/kg	122.0	0.6	2.2	200	96
55Mn	mg/kg	824	0.0	0.6	500	97
56Fe	mg/kg	7300	2.2	1.2		
59Co	mg/kg	3.3	4.1		500	96
60Ni	mg/kg	20.6	0.9	1.7	500	94
65Cu	mg/kg	486	0.4	2.6	250	93
66Zn	mg/kg	16	3.8	1.1	500	94
75As	mg/kg	1.6	4.9		40	96
82Se	mg/kg	9.64			10	99
107Ag	mg/kg	4.27				
111Cd	mg/kg	0.1			50	96
114Cd	mg/kg	0.2			50	95
121Sb	mg/kg	0.83			100	94
137Ba	mg/kg	31			2000	102
205Tl	mg/kg	0.872				
208Pb	mg/kg	26	2.3	2.8	20	94

Table 15 - Soil Digest Results

Most analytes in the Stony Soil were above 50*IDL and all show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction.

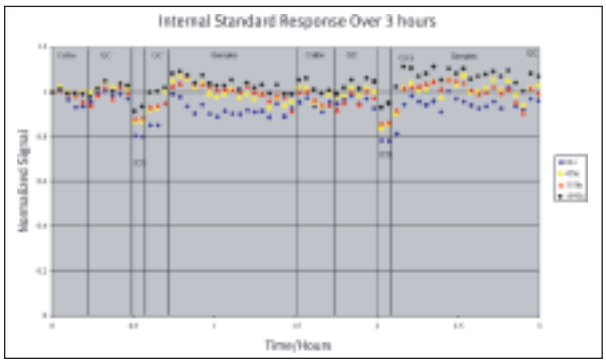
BIOTA DIGEST (N=9)						
ANALYTE	UNITS	SAMPLE RESULT	DUP (% RPD)	SER (% RPD)	SPIKE AMOUNT (µg/L)	SPIKE REC %
9Be	mg/kg	0.03			50	97
23Na	mg/kg	4700	0.5			
25Mg	mg/kg	510	0.3	4.7		
27Al	mg/kg	22			2000	96
39K	mg/kg	6940	1.2	0.5		
44Ca	mg/kg	400				
51V	mg/kg	1.0			500	96
52Cr	mg/kg	0.7			200	96
55Mn	mg/kg	4			500	97
56Fe	mg/kg	300				
59Co	mg/kg	0.8			500	96
60Ni	mg/kg	1.4			500	95
65Cu	mg/kg	21	1.1	0.6	250	95
66Zn	mg/kg	73	2.1	3.2	500	94
75As	mg/kg	2.3	3.0		40	94
82Se	mg/kg	6.80	5.7		10	97
107Ag	mg/kg	5.54				
111Cd	mg/kg	1.4			50	96
114Cd	mg/kg	1.5	0.2		50	94
121Sb	mg/kg	0.66			100	92
137Ba	mg/kg	5			2000	105
205Tl	mg/kg	0.276				
208Pb	mg/kg	1			20	94

Table 16 - Biota Digest Results

Very few analytes in the Biota digest sample were above 50*IDL and therefore few duplicate or serial dilution tests could be applied. Those that are, show relative percentage differences (RPDs) that are well within the allowable limit of 20 %. The spike recoveries in this matrix are well within the allowable range of 75-125 %. Silver was not tested on these spiked samples due to the presence of high chloride from the Aqua Regia extraction.

4.6 Internal Standard Response and Stability

Graph 1 shows the internal standard responses, (normalized to the initial response for the calibration blank) for a three-hour analytical duration, running real samples. It is seen that the overall drift during the two hour period is negligible and samples rarely produce internal standard responses outside of ±10 % of that of the initial calibration blank. It is also seen that the high matrix ICS solutions produce a fairly modest 10-20 % suppression.



Graph 1 - Internal Standard Response over a 2-Hour Period Running Calibration, QCs and Samples

5. Conclusions

The XSERIES 2 demonstrates SW-846 method 6020A compliant analysis for a wide range of sample types and easily copes with the stringent interference checks and AQC requirements of the method. A combination of specifically designed hardware and software tools enables and simplifies 6020A compliant analysis as outlined below.

Mass calibration and resolution checking is made simple with the custom Performance Report and peaks are easily set to the required width using the variable resolution function. The Performance Report also monitors and records the precision over five measurements, allowing a "Tune" sample to be tagged to each sample run. Any deviations from acceptable performance are clearly flagged in red and the report ends with a simple, unambiguous *Pass* or *Fail* statement.

The unique Xi interface design produces low background equivalent concentrations, resulting in very low instrument detection limits (as seen in Table 7). It reduces the effective contribution of polyatomic species allowing robust, reproducible interference correction (as seen in Table 11), and enhances stability when analyzing solutions containing high levels of matrix components, e.g. Ca, Na, Fe, Mg, K. This is demonstrated by the consistent CCV results (see Table 9) and the stability of the internal standards (see Graph 1). The unique response properties of this interface technology coupled with the dual mode simultaneous detector allow unrivalled linear range. This further improves productivity by reducing the number of dilutions required.

The PlasmaLab software has a built-in QC checking capability that is specifically designed to meet the requirements of EPA methods. Each QC type (ICV, CCV, LCS, etc) is available as a default in the QC set-up page and the user can also define their own QC tests, as required. The results display page visually flags results that are outside the allowed range making validation a simple process. Percentage recoveries can be automatically calculated for any QC sample or spiked sample and percentage differences can be calculated for DUP and SER samples. A variety of user-selectable automated actions can be set-up to ensure fully compliant analysis is achieved during an unattended run.

PlasmaLab enables automated initiation of measurement and completion of washout using the intelligent Monitored Uptake / Washout features. This reduces the amount of non-productive time and maximises useful analytical time. The productivity tools in PlasmaLab in combination with the rapidity of the XSERIES 2 quadrupole and the low-volume sample introduction system result in the fastest analysis with complete compliance. Samples in this study were being processed at a speed of 1 sample every 2 minutes and 45 seconds, or 22 samples per hour. This makes the XSERIES 2 the ultimate ICP-MS for cost-effective elemental analysis.

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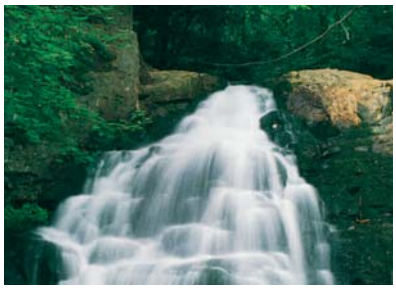
AN40619_E 03/07C

Product Specifications

The unique VP100 continuous flow vapor generation system offers exceptional performance, fast sample analysis and easy method development. The system achieves superb detection limits for hydride and cold vapor forming elements including mercury and arsenic.

VP100 Continuous Flow Vapor Generation System

Incredible performance in a user-friendly package



The Thermo Scientific iCE 3000 Series AA spectrometers combined with the VP100 accessory enables you to achieve detection limits comparable to an ICP-MS, but at a fraction of the cost.

- **Fast Analysis**
  Analysis of a typical sample is possible in less than 60 seconds. The VP100's unique continuous flow design means that sample wash-out time is reduced and sample throughput is increased.
- **Superb performance**
  An iCE 3000 Series AA and VP100 accessory can give you detection limits in the parts per trillion range for several important hydride and cold vapor forming elements: As, Se, Ge, Bi, Pb, Te, Sb, Sn, and Hg.
- **Fully customizable**
  The VP100 can be optimized to meet the exact needs of the user. With simple, software-controlled adjustments you will quickly be able to find the perfect balance of speed and sensitivity for your analysis.
- **User-friendly**
  All the tubing and connections on the VP100 are color-coded, making set-up of the accessory quick and easy. The unique design removes the need for switching-valves and makes the analysis simpler for the user. The VP100 is entirely controlled by the SOLAAR software, so any adjustments to instrument parameters can be made using SOLAAR's intuitive user interface.
- **Easy to maintain**
  The unique continuous flow system ensures self-cleaning of the VP100. The only maintenance required is to wash the system with de-ionized or distilled water when an analysis is complete.

Product Specifications

Principle of Operation

Hydride generation AAS uses a chemical reaction to create volatile metal-hydride species which can be analyzed in the vapor phase. Suitable liquid reagents are mixed with samples in a reaction zone to form hydride vapor. The vapor is separated from the liquid mixture in a gas-liquid separator and carried to an atomization cell which can be heated if required. When heated, the hydride decomposes to release atoms, which are then measured by atomic absorption. The cell can either be heated using the air-acetylene flame or by an electrically heated furnace. For the analysis of mercury, no heating is required as the chemicals used form elemental mercury, which passes as a vapor to the cell.

Performance

The VP100 vapor generation accessory combined with the iCE 3000 Series AA Spectrometers enables part per trillion level detection of hydride and vapor-forming elements. Table 1 gives typical detection limits for some commonly analyzed elements. These figures are comparable with those obtained via ICP-MS. In addition, the figures are likely to be more reliable for arsenic and selenium due to the removal of common ICP-MS interferences for those elements.

	Characteristic Concentration µg/L	Detection Limit µg/L
Antimony	0.29	0.06
Arsenic	0.2	0.05
Bismuth	0.36	0.1
Mercury	0.26	0.06
Selenium	0.7	0.15
Tellurium	0.46	0.1
Tin	0.38	0.2

Table 1. Typical detection limits achievable with the VP100 Vapor Generation Accessory and iCE 3000 Series AA Spectrometers

Intelligent Design

The VP100 has been designed to make vapor analysis as fast, simple and sensitive as possible. A unique, continuous flow design reduces wash-out times and eliminates carry-over. The gas-liquid separator is made from advanced materials that are completely inert to all reagents to reduce interferences and prolong its lifetime. All connections on the VP100 are color-coded to make set-up and maintenance simple.

Precision

Our use of state-of-the-art, mass-flow controlled gas supplies means that the VP100 is not reliant upon older, less accurate gas systems. This means that we can precisely control the carrier gas flow through the VP100. The accurate and precise mass-flow controlled system provides exceptional long-term stability, ensuring that gas flow rates do not change even if laboratory temperature or pressure varies.

EC90

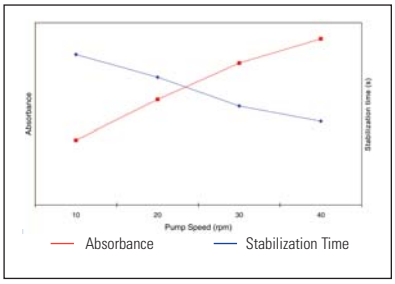
The electrically heated atomization cell (EC90) can be used in conjunction with the VP100. It provides better sensitivity and lower running costs compared to standard flame heating.

Specialized measurement kits

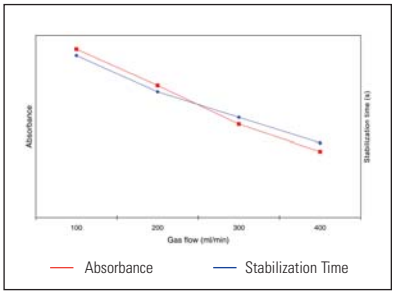
To ensure that the best performance is achieved for each of the hydride-forming elements we have included two different measurement cells. The T-cell is used for As, Se, Ge, Bi, Pb, Te, Sb and Sn. This silica cell is incredibly temperature-resistant, which means that it can be heated to the optimal temperatures to degrade the metal hydrides formed in the VP100. Mercury is analyzed using a special mercury cell, specifically designed with a longer path length to allow you to achieve the lowest possible detection limits.

Flexible analysis

The VP100 parameters can be adjusted using the software to allow you to fully optimize your analysis. Carrier gas flow and pump speed can be varied independently, which allows you to find the perfect balance between speed and sensitivity.



Graph 1: Pump speed vs Absorbance and Stabilization Time



Graph 2: Gas Flow vs Absorbance and Time

Conclusion

- The VP100 is a powerful tool for the measurement of hydride-forming elements, achieving exceptionally low detection limits
- Its unique design provides fast, repeatable and accurate analyses
- The VP100 is fully controlled by the Thermo Scientific SOLAAR software, eliminating manual optimization and making method development quick and user-friendly

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Consider this example of potential tax savings:

Equipment investment	$50,000
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Total 2010 tax year deduction	$50,000
Potential 2010 tax savings for a hospital in the 35% tax bracket	$15,000

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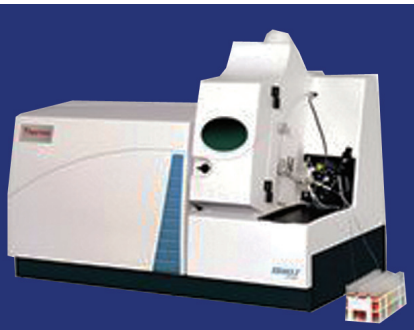

EXTENDED! Tax Benefits for 2010

You may be able to write off the entire cost of equipment purchases in 2010!

- You can take further advantage of the IRS Section 179 expense allowance to accelerate the write-off of equipment you acquire via capital lease in 2010. This can improve your cash flow by reducing your outlay of tax dollars in 2010.
- This expense allowance is $250,000 for 2010, **as recently extended by the HIRE Act of 2010.**
- Capital equipment investment above $250,000 is also eligible for standard MACRS depreciation.
- The Section 179 allowance is available for taxpayers with total capital investments of up to $800,000.
- This allowance applies to units contracted and placed into service through December 31, 2010.

Consider this example of potential tax savings:

Equipment Investment	$128,000
1st year Section 179 allowance	$250,000
Total 1st year deduction	$128,000
Potential 1st year tax savings for a business in the 35% tax bracket	$44,800

*Based on standard MACRS depreciation taken over five years on the balance of equipment investment less Section 179 allowance.

How can you realize tax savings from Section 179?

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