CCQM Key Comparison – Organic Solutions
CCQM-K47 Volatile Organic Compounds in Methanol
Final Report

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Introduction

At the October 2005 CCQM Organic Analysis Working Group Meeting (IRMM, Belgium), the decision was made to proceed with a Key Comparison study (CCQM-K47) and a concurrent subsequent pilot study (CCQM-P61.1) addressing the calibration function for the determination of volatile organic compounds (VOCs) used for water quality monitoring. Both studies were coordinated by CENAM and NIST. Benzene, *o*-xylene, *m*-xylene, and *p*-xylene were chosen as representative VOCs. The solvent of choice was methanol. This report summarizes the results for CCQM-K47.

Summary of Pilot Study CCQM-P61

At the October 2004 CCQM Organic Analysis Working Group Meeting (NRCCRM, China), the decision was made to proceed with a pilot study addressing the calibration function for the determination of volatile organic compounds (VOCs) used for water quality monitoring. Benzene, toluene, ethylbenzene, and three xylene isomers were chosen as representative VOCs. The solvent of choice was methanol. The pilot study CCQM-P61 Volatile Organic Compounds in Methanol was coordinated by CENAM and NIST.

Each CCQM-P61 participant received five ampoules of the a gravimetrically prepared solution. Each 2 mL ampoule contained approximately 1.2 mL of a methanol solution including benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene at concentrations between 13.37 µg/g (*o*-xylene) to 49.55 µg/g (toluene). The instructions requested the analysis of duplicate subsamples from each of four ampoules using the laboratory's analytical procedure for determination of the mass fraction concentrations of the target analytes.

Nineteen laboratories received samples for CCQM-P61; eighteen laboratories reported measurement results to the coordinators. Two laboratories used IDMS, six laboratories used internal standards, six laboratories used external standards, and the other four laboratories did not report the method of quantification used. Most of the laboratories used gas chromatography with mass spectrometry (GC/MS) and/or GC with flame ionization detection (GC-FID).

The majority of reported results agreed with the gravimetric preparation values to within ± 5 %, with a minority of values ranging up to ± 20 %.

Design, Conduct, and Results from CCQM-K47

Study Material

The material used in CCQM-K47 was similar to that used in the CCQM-P61 pilot study: a gravimetrically prepared methanol solution of the four target VOCs (benzene and the three xylene isomers) plus toluene and ethylbenzene. The solution was prepared from neat materials procured from commercial sources. The purities of the starting materials were determined by GC-FID. Table 1 lists the gravimetric preparation impurity-adjusted mass fraction of the target VOCs in the study solution.

Table 1. Gravimetric Preparation Mass Fraction and Homogeneity Evaluation of Target VOCs

	Mass Fraction, µg/g		ANOVA	
Analyte	Value	U_{95}(Value)	F_c	F_t
benzene	39.40	0.39	1.83	2.39
o-xylene	15.77	0.28	1.39	2.39
m-xylene	20.87	0.20	1.16	2.39
p-xylene	28.25	0.28	1.04	2.39

Homogeneity Evaluation

Table 1 also summarizes the results of an Analysis of Variance (ANOVA) homogeneity evaluation for the target VOCs. Ten ampoules (A043, A073, A173, A203, A373, A381, A486, A502, A579, A581) were measured in triplicate using GC-FID. The null hypothesis was that the measurement means in all of the ampoules are identical; the alternate hypothesis was that the mean in at least one of the ampoules differed from the others. For all four of the target VOCs, the null hypothesis of homogeneity is accepted. The relative standard deviation of the measurements ranged from 0.2 % to 0.5 %.

Study Design

Each participant in CCQM-K47 received five ampoules of the study solution. Each 2-mL ampoule contained approximately 1.2 mL of solution. Participants were informed that the mass fractions of all target VOCs ranged between 10 µg/g and 50 µg/g. Participants were requested to analyze duplicate aliquots from each of four ampoules using an analytical procedure validated in CCQM-P61.

Participants

The eight laboratories listed in Table 2 received samples for CCQM-K47. All eight laboratories reported measurement results to the coordinators.

Table 2. CCQM-K47 Participants

NMI	Submitted by	Country	Email Contact
BAM	Tin Win, Rosemarie Philipp, Katja Kaminski	Germany	tin.win@bam.de
CENAM	Mauricio Maldonado Torres, Evangelina Camacho Frías, Melina Pérez Urquiza	México	meperez@cenam.mx
INTI	Adriana Rosso	Argentina	mariare@inti.gov.ar, cpuglisi@inti.gov.ar
KRISS	Dal Ho Kim	Korea	byungjoo@kriss.re.kr
NIST	Michele Schantz	USA	michele.schantz@nist.gov
NMIJ	K. Ishikawa	Japan	ishikawa-keiichiro@aist.go.jp
VNIIM	A.I. Krylov, Y.A. Kustikov	Russia	lkonop@b10.vniim.ru
VSL	Annarita Baldan	Netherlands	abaldan@nmi.nl

Analytical Methods

Table 3 summarizes the analytical methods used by the eight participants. Table 4 summarizes the amount of sample used in each analysis. Tables 5 and 6 summarize the materials used to prepare calibration solutions. Table 7 summarizes how the calibration solutions were used.

Table 3. Analytical Methods

		Column			
NMI	Method	Phase	L, m	ID, mm	FT, µm
BAM	GC/MS: benzene, *o*-xylene, *m&p*-xylene (coelution)	DB-624	30	0.32	1.8
	GC-FID: *m*/*p*-xylene ratio	DB-WAX	60	0.32	0.5
CENAM	GC/MS	DB-WAX	60	0.25	0.25
INTI	GC-FID	PEG (Supelcowax)	60	0.32	0.5
KRISS	GC-FID	PEG (5% phenyl) methyl polysiloxane	30	0.53	1 2.65
NIST	GC-FID: xylenes	DB-WAX	15	0.45	0.85
	GC/MS: benzene	DB-VRX	60	0.25	1.4
NMIJ	GC/MS	DB-WAX	60	0.32	0.5
VNIIM	GC/MS	HP 5 MS	30	0.25	0.25
VSL	GC-FID	CPWAX 52	60	0.53	2

Table 4. Sample Mass of CCQM-K47 Solution used for Analysis

NMI	Mass solution used, g
BAM	0.05 to 0.09
CENAM	0.3
INTI	0.5
KRISS	0.2
NIST	0.4
NMIJ	0.4
VNIIM	0.5
VSL	0.7

Table 5. Certified Reference Materials Used as Calibrants

			Certified Mass Fraction, µg/g			
NMI	Solvent	Source	benzene	*o*-xylene	*m*-xylene	*p*-xylene
BAM	Methanol	KRISS	40.6 ±0.6	102.0±1.6	100.2±0.6	100.2±0.6

Table 6. Neat Materials Used to Prepare Calibrants

NMI	Source	Mass Fraction, mg/g benzene	*o*-xylene	*m*-xylene	*p*-xylene
CENAM	Aldrich	0.9988	0.9915	0.9968	0.9967
INTI	Merck	>0.99			
INTI	AnalityCals Carlo Erba		0.988	0.978	>0.99
KRISS	Sigma-Aldrich	0.9995	0.9916	0.9977	0.9986
NIST	Sigma Aldrich	1.00	0.9363	1.00	0.9924
NMIJ	NIM CRM 4002-a *	0.99996			
NMIJ	NIM CRM 4011-a *		0.9994		
NMIJ	NIM CRM 4012-a *			0.9981	
NMIJ	NIM CRM 4013-a *				0.9988
VNIIM	SOP 0003-03 STC	0.9997			
VNIIM	SOP 0020-03 STC		0.997		
VNIIM	SOP 0015-03 STC			0.9966	
VNIIM	SOP 0016-03 STC				0.999
VSL	Aldrich	0.999			
VSL	Fluka		0.995	0.995	0.995

* Deuterated Certified Reference material

Table 7. Calibration Method used, Number of Calibration Levels, and Calibration Range

			benzene		o-xylene		m,p-xylene	
NMI	Use	Internal standard was added	#	mg/g	#	mg/g	#	mg/g
BAM	Internal	at 2nd of 2 dilutions	5	0.3 - 4.8	5	0.7 - 12.0	5	0.7 - 12.0
CENAM	Internal	before injection	5	1 - 60	5	1 - 60	5	1 - 60
INTI	External		4	3.5 - 53	3	3.5 - 53	3	3.5 - 53
KRISS	External		1		1		1	
NIST	Internal	during sample preparation	1		1		1	
NMIJ	IDMS	to sample (deuterated VOC)						
VNIIM	Internal	before subsample analysis	1		1		1	
VSL	Internal	to autosampler vials	6	4 - 60	6	1 - 35	6	1 - 35

Results

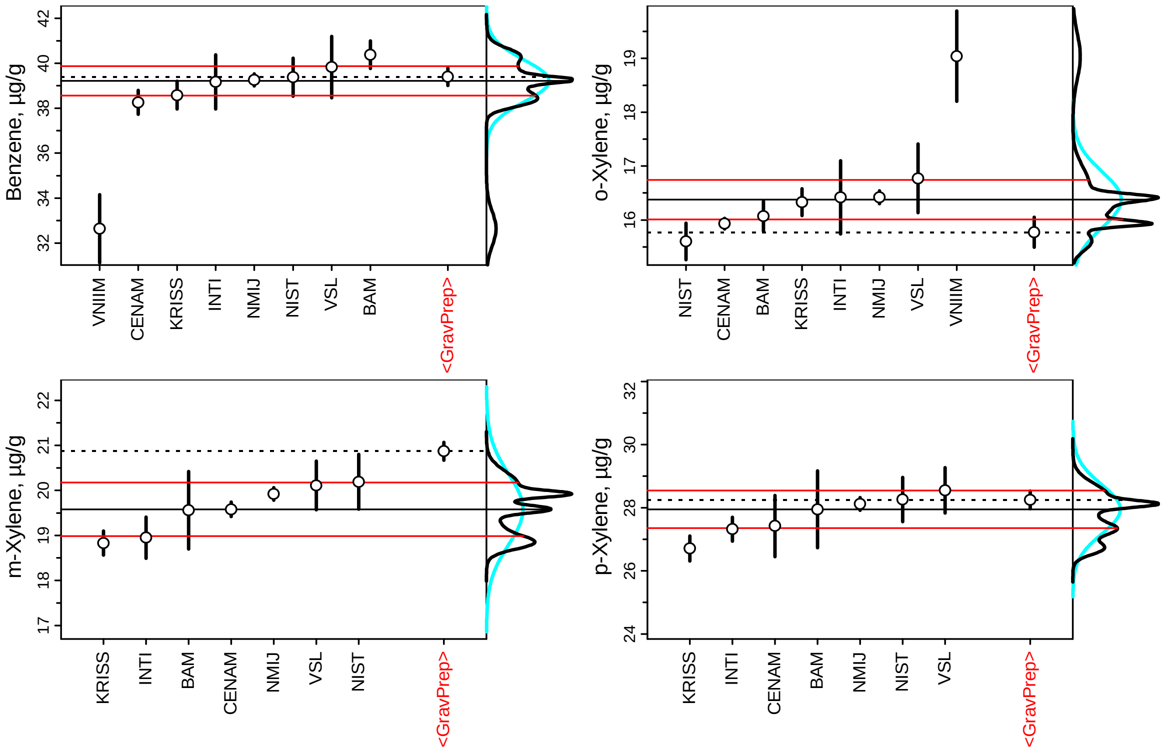
The values, the combined uncertainties on the values, u, and the 95 % expanded uncertainties, U_{95}, as submitted by the participants are summarized in Table 8 and displayed in Figure 1. Each panel of Figure 1 displays the results, their consensus summary, and the gravimetric preparation values for one of the target VOCs. Each “dot” denotes a value and each vertical “bar” denotes the 95% confidence interval on the value. The solid black horizontal line represents the consensus median, the red horizontal lines represent the robust 95 % confidence interval about the median, and the dotted black line goes through the gravimetric value. The black curve to the right of each panel is the additive probability density function for the reported results; the light blue curve is the Gaussian defined by the consensus summary values. In all four panels, the mass-fraction axis spans a 30 % interval about the consensus value.

Table 8. Submitted Values, µg/g

NMI	benzene			*o*-xylene			*m*-xylene			*p*-xylene		
	Value	u	U_{95}	Value	u	U_{95}	Value	u	U_{95}	Value	u	U_{95}
BAM	40.38	0.31	0.62	16.07	0.14	0.28	19.56	0.43	0.86	27.95	0.61	1.22
CENAM	38.26	0.27	0.53	15.93	0.05	0.10	19.58	0.08	0.16	27.42	0.48	0.97
INTI	39.17	0.49	1.21	16.42	0.24	0.68	18.95	0.16	0.46	27.32	0.16	0.38
KRISS	38.58	0.31	0.62	16.33	0.12	0.25	18.83	0.13	0.27	26.71	0.20	0.40
NIST	39.38	0.43	0.85	15.60	0.17	0.34	20.19	0.29	0.61	28.26	0.35	0.70
NMIJ	39.26	0.14	0.27	16.42	0.06	0.12	19.92	0.07	0.14	28.12	0.10	0.20
VNIIM	32.64	0.76	1.52	19.04	0.42	0.84	Reported as sum of *m*- & *p*-xylene					
VSL	39.83	0.69	1.37	16.77	0.32	0.64	20.11	0.27	0.54	28.55	0.36	0.72
Consensus*	39.22	0.33	0.76	16.38	0.18	0.42	19.58	0.30	0.70	27.95	0.30	0.70

* Robust consensus values calculated as: Value = median, u = median absolute deviation from the median (MADe), and $U_{95} = u * t_{0.025,n-1}$ where $t_{0.025,n-1}$ is the two-sided Student's t for 95 % confidence and n measurements.

Figure 1. Dot-and-Bar Plots for the Four Target VOCs



Additional information on the methods and uncertainty calculations used by the participants is included in Appendix A. Representative chromatograms are provided in Appendix B.

Key Comparison Reference Values

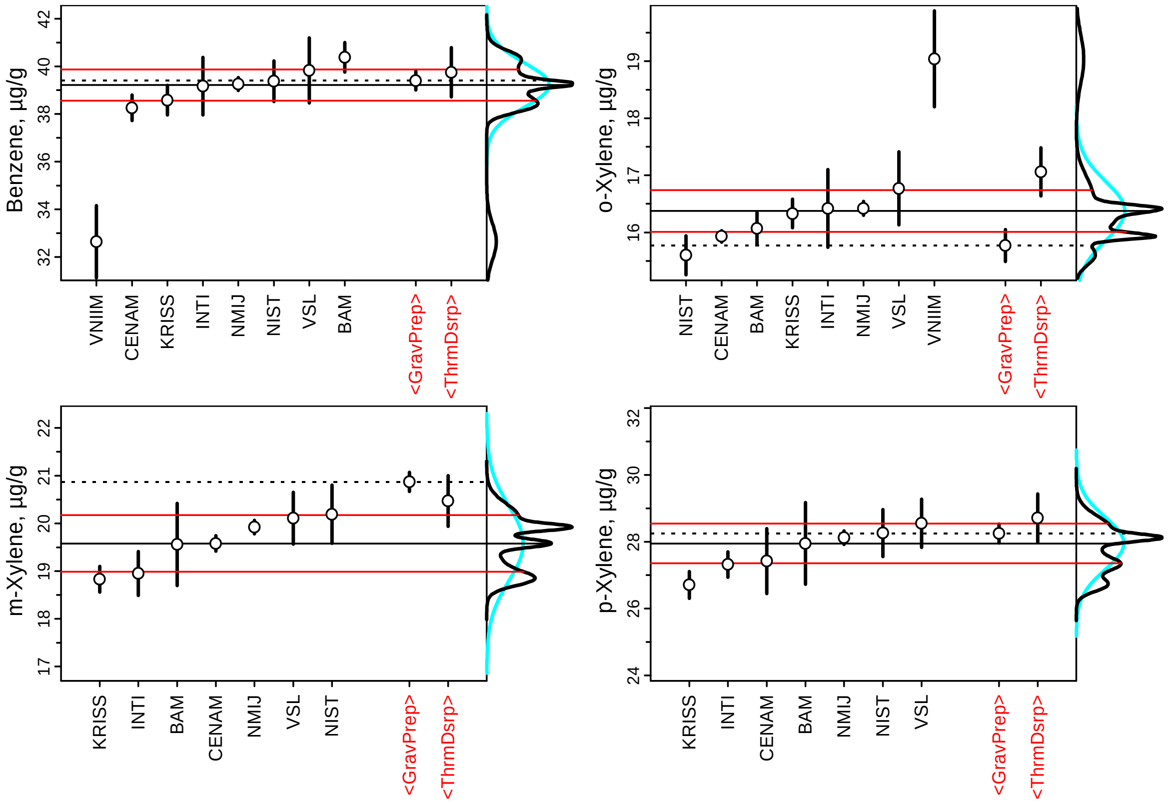
As displayed in Figure 1, the consensus summary values agree well with the gravimetric preparation values for benzene and *p*-xylene but not for *o*-xylene nor *m*-xylene. Review of the solution preparation records failed to identify any experimental or data analysis oversight. Inspection of the chromatograms in Appendix B suggests that discrepancy for *m*-xylene is not caused by insufficient chromatographic separation of *m*- and *p*-xylene.

At the April 2006 CCQM Meeting in Paris, VSL was asked to analyze the CCQM-47 solution with thermal desorption GC-FID. Dynamic dilution was used to prepare six calibration levels of gas mixtures following the procedure of ISO 6145-8. These reference gas mixtures were loaded onto tenax TA sorbent tubes. The CCQM-K47 solution was loaded onto tenax TA sorbent tubes using a calibrated 10 µL syringe, three tubes each for five ampoules. Table 9 summarizes the results of this evaluation; Figure 2 displays the results relative to the measurement and gravimetric preparation values

Table 9. Results from VSL Thermal Desorption Analysis, µg/g

benzene		*o*-xylene		*m*-xylene		*p*-xylene		toluene	
Value	U_{95}	Value	U_{95}	Value	U_{95}	Value	U_{95}	Value	U_{95}
39.75	1.03	17.06	0.42	20.47	0.53	28.71	0.72	20.80	0.53

Figure 2. Dot-and-Bar Plots for the Four target VOCs with VSL Thermal Desorption Results



The thermal desorption results agree well with the gravimetric preparation values for benzene, *m*-xylene, and *p*-xylene. The result for *o*-xylene does not agree well with either the gravimetric or consensus value.

At the April 2008 CCQM Meeting in Paris, consideration was given to defining the Key Comparison Reference Value (KCRV) from the consensus, gravimetric preparation, thermal desorption, or some combination of the three values. Consideration was also given to voiding the study completely and to dropping *o*-xylene as a target measurand. On the basis of the agreement between the gravimetric preparation and thermal desorption values for *m*-xylene and the absence of any evidence of an analytical blunder that would be specific to *o*-xylene, the decision was made to accept the complete study as valid and use the gravimetric preparation values as the KCRV for all for four target VOCs.

Key Comparison Reference Value Uncertainties

Recognizing that the uncertainty estimated from the gravimetric preparation process may not fully represent the variability of the VOC levels in the solution levels as delivered to the participants, the combined uncertainty for the KCRV is estimated as:

$$\begin{aligned} u(\mathrm{KCRV}) &= \sqrt{u^2(\mathrm{GravPrep}) + s^2(\mathrm{Consensus})} \\ s(\mathrm{Consensus}) &= \mathrm{MADe}/\sqrt{n} \end{aligned} .$$

where MADe is a robust estimate for the standard deviation of the n reported values. The 95 % level of confidence expanded uncertainty is estimated with the standard metrological factor, k=2:

$$U_{95}(\mathrm{KCRV}) = 2 \cdot u(\mathrm{KCRV}) \ .$$

Table 10 lists the KCRV, u(KCRV), and U_{95}(KCRV) values for the four target VOCs.

Table 10. Key Comparison Reference Values and Their Uncertainties, µg/g

VOC	KCRV	u(KCRV)	U_{95}(KCRV)
benzene	39.4	0.4	0.8
o-xylene	15.8	0.2	0.5
m-xylene	20.9	0.3	0.6
p-xylene	28.3	0.3	0.7

Degrees of Equivalence

Since participant results are not used in the estimation of the KCRV, the degree of equivalence for a given participant value for a given VOC, $d \pm U_{95}(d)$, is estimated as:

$$d = \mathrm{Value} - \mathrm{KCRV}; \quad u(d) = \sqrt{u^2(\mathrm{Value}) + u^2(\mathrm{KCRV})}; \quad U_{95}(d) = 2 \cdot u(d); \quad Rd = d/u(d)$$

where Value and u(Value) are the participant's reported value and combined uncertainty. Table 11 lists the degrees of equivalence for the four target VOCs.

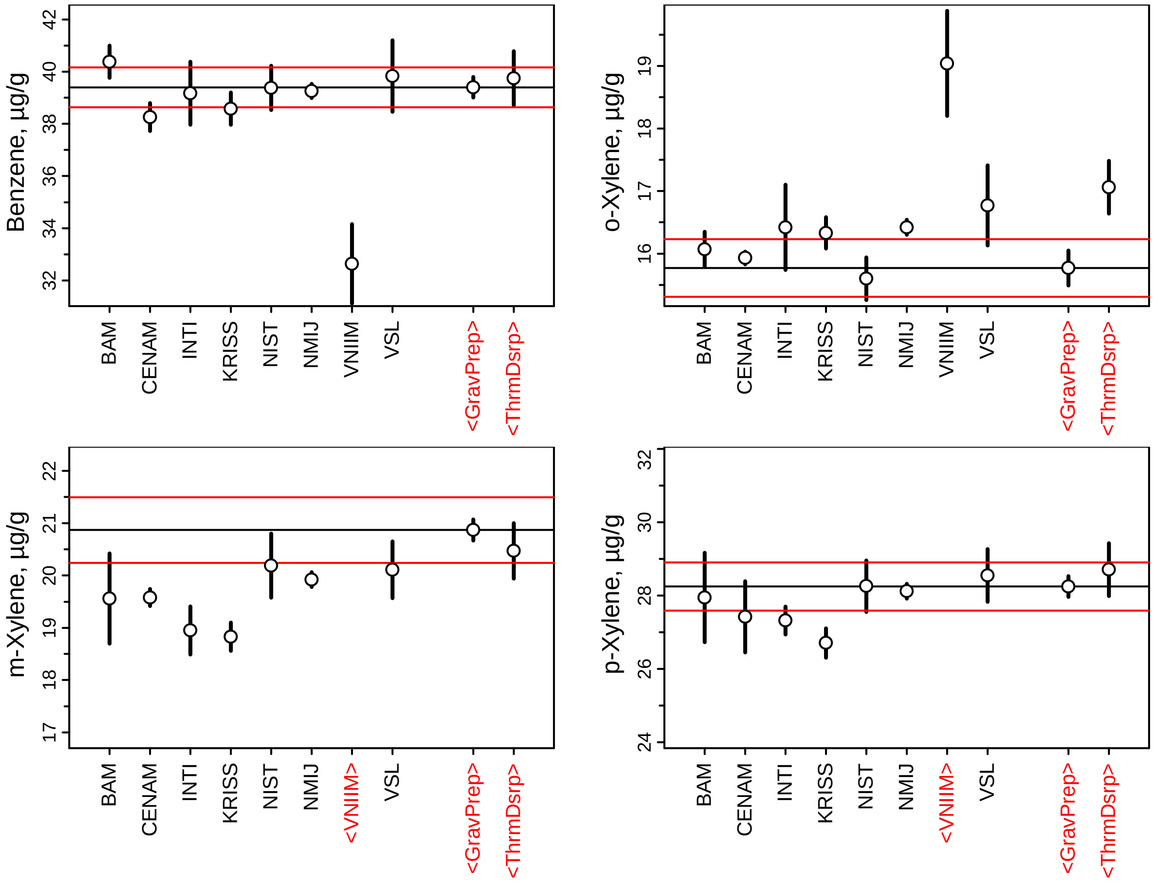
Table 11. Degrees of Equivalence

	benzene			*o*-xylene			*m*-xylene			*p*-xylene		
NMI	*d*	U_{95}	*Rd*	*d*	U_{95}	*Rd*	*d*	U_{95}	*Rd*	*d*	U_{95}	*Rd*
BAM	1.0	1.0	2.0	0.3	0.5	1.1	-1.3	1.1	-2.5	-0.3	1.4	-0.4
CENAM	-1.1	0.9	-2.5	0.2	0.5	0.7	-1.3	0.6	-4.0	-0.8	1.2	-1.4
INTI	-0.2	1.4	-0.3	0.7	0.8	1.6	-1.9	0.8	-4.9	-0.9	0.8	-2.5
KRISS	-0.8	1.0	-1.7	0.6	0.5	2.1	-2.0	0.7	-6.0	-1.5	0.8	-4.0
NIST	0.0	1.1	0.0	-0.2	0.6	-0.6	-0.7	0.9	-1.6	0.0	1.0	0.0
NMIJ	-0.1	0.8	-0.3	0.7	0.5	2.7	-0.9	0.6	-3.0	-0.1	0.7	-0.4
VNIIM	-6.8	1.7	-8.0	3.3	1.0	6.8						
VSL	0.4	1.6	0.5	1.0	0.8	2.5	-0.8	0.8	-1.8	0.3	1.0	0.6

Values of *Rd* less than -2 or greater than +2 indicate results that deviate from the KCRV by more than is likely given the estimated uncertainties.

Figure 3 provides an approximate graphical display of the degrees of equivalence. Note that in the panels of this Figure the participant results are listed in alphabetical order, the solid black line represents the KCRV, and the solid red lines bound the symmetric interval KCRV ±U_{95}(KCRV).

Figure 3. Approximate Degrees of Equivalence

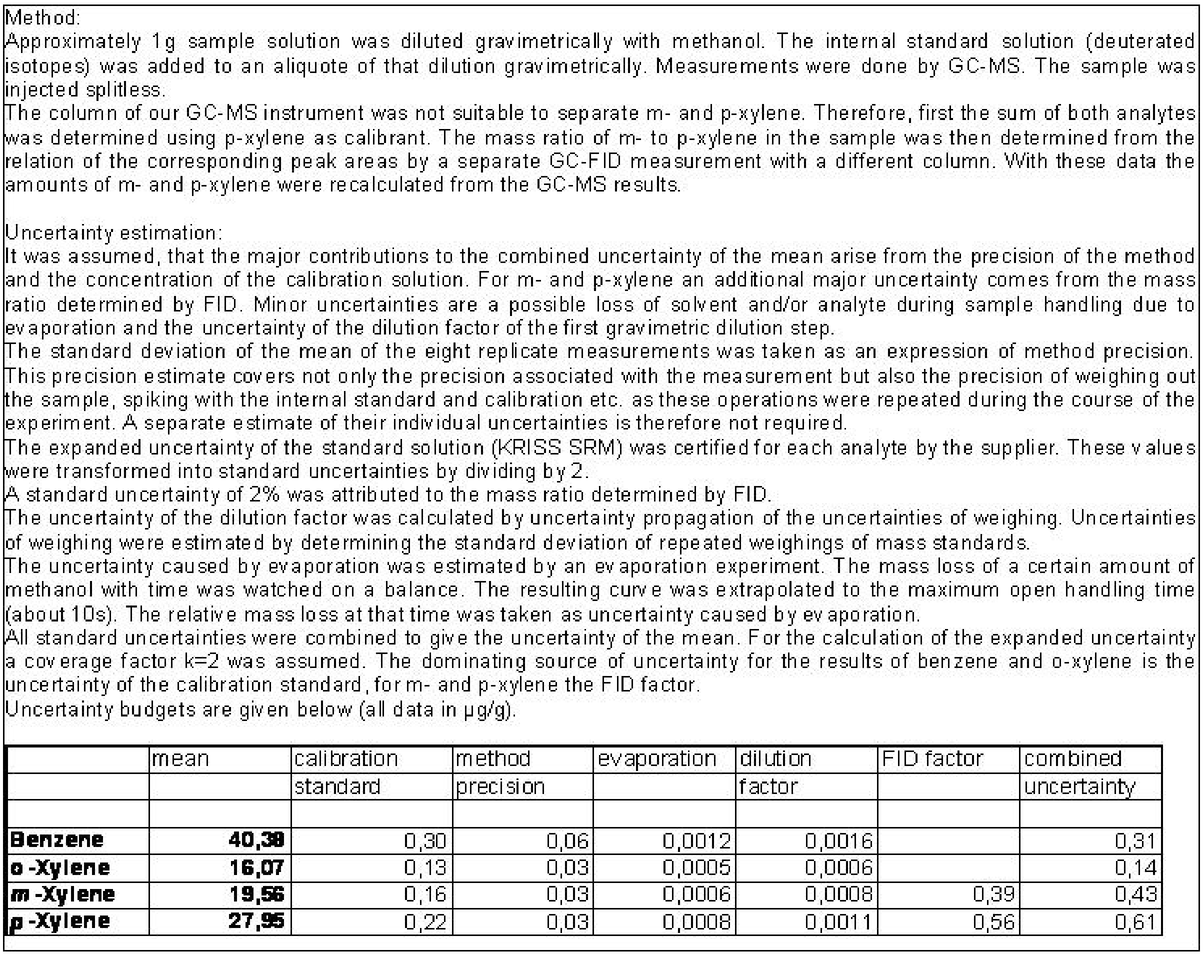


How Far Does the Light Shine?

Key Comparison CCQM-K47 demonstrated the capabilities of participating NMIs to identify and measure the four target VOCs benzene, *o*-xylene, *m*-xylene, and *p*-xylene in a calibration solution using GC-based methods. These measurands were selected to be representative of VOCs monitored in water quality assessments. The measurement challenges in CCQM-K47, such as avoiding volatility loss, achieving adequate chromatographic resolution, and isolating potential interferences, are typical of those required for value-assigning volatile reference materials. Participants achieving comparable measurements for all four VOCs in this Key Comparison should be capable of providing reference materials and measurements for VOCs in solutions when present at concentration levels greater than 10 µg/g.

Appendix A: NMI Reports

BAM



Method:
Approximately 1g sample solution was diluted gravimetrically with methanol. The internal standard solution (deuterated isotopes) was added to an aliquote of that dilution gravimetrically. Measurements were done by GC-MS. The sample was injected splitless.
The column of our GC-MS instrument was not suitable to separate m- and p-xylene. Therefore, first the sum of both analytes was determined using p-xylene as calibrant. The mass ratio of m- to p-xylene in the sample was then determined from the relation of the corresponding peak areas by a separate GC-FID measurement with a different column. With these data the amounts of m- and p-xylene were recalculated from the GC-MS results.

Uncertainty estimation:
It was assumed, that the major contributions to the combined uncertainty of the mean arise from the precision of the method and the concentration of the calibration solution. For m- and p-xylene an additional major uncertainty comes from the mass ratio determined by FID. Minor uncertainties are a possible loss of solvent and/or analyte during sample handling due to evaporation and the uncertainty of the dilution factor of the first gravimetric dilution step.
The standard deviation of the mean of the eight replicate measurements was taken as an expression of method precision. This precision estimate covers not only the precision associated with the measurement but also the precision of weighing out the sample, spiking with the internal standard and calibration etc. as these operations were repeated during the course of the experiment. A separate estimate of their individual uncertainties is therefore not required.
The expanded uncertainty of the standard solution (KRISS SRM) was certified for each analyte by the supplier. These values were transformed into standard uncertainties by dividing by 2.
A standard uncertainty of 2% was attributed to the mass ratio determined by FID.
The uncertainty of the dilution factor was calculated by uncertainty propagation of the uncertainties of weighing. Uncertainties of weighing were estimated by determining the standard deviation of repeated weighings of mass standards.
The uncertainty caused by evaporation was estimated by an evaporation experiment. The mass loss of a certain amount of methanol with time was watched on a balance. The resulting curve was extrapolated to the maximum open handling time (about 10s). The relative mass loss at that time was taken as uncertainty caused by evaporation.
All standard uncertainties were combined to give the uncertainty of the mean. For the calculation of the expanded uncertainty a coverage factor k=2 was assumed. The dominating source of uncertainty for the results of benzene and o-xylene is the uncertainty of the calibration standard, for m- and p-xylene the FID factor.
Uncertainty budgets are given below (all data in µg/g).

	mean	calibration standard	method precision	evaporation	dilution factor	FID factor	combined uncertainty
Benzene	**40,38**	0,30	0,06	0,0012	0,0016		0,31
o -Xylene	**16,07**	0,13	0,03	0,0005	0,0006		0,14
***m* -Xylene**	**19,56**	0,16	0,03	0,0006	0,0008	0,39	0,43
***p* -Xylene**	**27,95**	0,22	0,03	0,0008	0,0011	0,56	0,61

CENAM

Uncertainty was calculated by using ISO-GUM guide 1993 "Quantifying Uncertainty in Analytical Measurement" standard deviation between ampoules, same ampoule standard deviation, calibration curve error and uncertainty by solvent purity was combined and the combined uncertainty multiplied by k=2.

INTI

Uncertainty estimated from the calibration curve (sample variability agrees with the variability of the calibration curve

KRISS

Source of Uncertainty	**Relative standard uncertainty (rel %) from each Source**			
	Benzene	***o-Xylene***	***m-Xylene***	***p-Xylene***
Standard Solution (rel%)	**0.55%**	**0.50%**	**0.56%**	**0.56%**
Purity (rel%)	0.005%	0.005%	0.008%	0.005%
Repeatability of gravimetric dilution of Stock solution (rel%)	0.52%	0.44%	0.18%	0.18%
Repeatability of gravimetric preparation of Stock solution	0.04%	0.24%	0.53%	0.53%
Measurement (rel%)				
Repeatability of anaylsys(Within sampl	0.1-0.8%	0.1-0.8%	0.1-0.8%	0.1-0.8%
Between sample	0.21-0.22%	0.03-0.15%	0.06-0.28%	0.09-0.32%
Combined Uncertainty	**0.79%**	**0.75%**	**0.71%**	**0.74%**
Expended Uncertainty(95%)	**1.61%**	**1.52%**	**1.43%**	**1.49%**

NIST

	benzene	o-xylene	m-xylene	p-xylene	degrees of freedom
Measured Value (mean)	39.38	15.60	20.19	28.26	
Uncertainty Components					
Measurement of Samples	0.177	0.070	0.214	0.208	7
Measurement of Calib Stds	0.002	0.001	0.001	0.006	5
purity of compounds used for prep of calibration solutions	0.002	0.003	0.001	0.001	2
Conc of Calib Soln	0.394	0.156	0.202	0.283	inf
Combined Standard Unc.	0.432	0.171	0.294	0.351	
Effective degrees of freedom	249	254	25	56	
k (from t-distribution)	1.97	1.97	2.06	2.00	
Expanded Uncertainty	0.85029	0.34	0.61	0.70	
Expanded Unc as %	2.16%	2.16%	3.00%	2.49%	

NMIJ

Analyte C_X (ug/g):

$$C_X = \left(\frac{R_{sample} \times M_Z \times C_{calib} \times M_{YSmp}}{R_{std} \times M_X \times M_{YStd}} \right)$$

Rsample	Analyte/D-analyte ratio for sample blend
Rstd	Analyte/D-analyte ratio for standard blend
Mx	Weight of sample solution (g)
Mz	Weight of standard solution (g)
MYSmp	Weight of spike solution (g) added to sample solution
MYStd	Weight of spike solution (g) added to standard solution
Ccalib	Concentration of calibration solution (ug/g)

NMIJ: Benzene

Parameter	**Source of Uncertainty**	**X_i**		**$U(x_i)$**		**(∂f/∂xi)**	**(∂f/∂xi)u(xi)**	**Degrees of Freedom (ν_i)**	**Type**	**Source of Data**
P_{method}	Precision for the entire method	39.26	ug/g	0.02	ug/g	1	0.0160	39	A	Replicate analysis of the 4 ampoules
R_{sample}	Measurement of Rsample	1.15		Covered within P_{method}		-	-	-	-	-
$R_{standard}$	Measurement of Rstd	1.05		Covered within P_{method}		-	-	-	-	-
$M_{Z\ (L)}$	Balance linearity	0.42	g	0.0003	g	93.477	0.028	Large	B	Balance calibration certificate
C_{calib}		39.3	ug/g	0.09825	ug/g	0.999	0.0982	Large	B	Supplier's specification
$M_{Ysmp\ (L)}$	Balance linearity	0.2	g	0.0003	g	196.303	0.0589	Large	B	Balance calibration certificate
$M_{Ystd\ (L)}$	Balance linearity	0.2	g	0.0003	g	-196.303	-0.0589	Large	B	Balance calibration certificate
$M_{X\ (L)}$	Balance linearity	0.44	g	0.0003	g	-89.228	-0.0268	Large	B	Balance calibration certificate

NMIJ: o-xylene

Parameter	**Source of Uncertainty**	**X_i**		**$U(x_i)$**		**(∂f/∂xi)**	**(∂f/∂xi)u(xi)**	**Degrees of Freedom (ν_i)**	**Type**	**Source of Data**
P_{method}	Precision for the entire method	16.42	ug/g	0.01	ug/g	1	0.0128	39	A	Replicate analysis of the 4 ampoules
R_{sample}	Measurement of Rsample	1.07		Covered within P_{method}		-	-	-	-	-
$R_{standard}$	Measurement of Rstd	1.08		Covered within P_{method}		-	-	-	-	-
$M_{Z\ (L)}$	Balance linearity	0.42	g	0.0003	g	39.095	0.012	Large	B	Balance calibration certificate
C_{calib}		16.6	ug/g	0.0415	ug/g	0.989	0.0410	Large	B	Supplier's specification
$M_{Ysmp\ (L)}$	Balance linearity	0.2	g	0.0003	g	82.099	0.0246	Large	B	Balance calibration certificate
$M_{Ystd\ (L)}$	Balance linearity	0.2	g	0.0003	g	-82.099	-0.0246	Large	B	Balance calibration certificate
$M_{X\ (L)}$	Balance linearity	0.44	g	0.0003	g	-37.318	-0.0112	Large	B	Balance calibration certificate

uc= 0.06

NMIJ: *m*-xylene

Parameter	Source of Uncertainty	X_i		$U(x_i)$		(∂f/∂xi)	(∂f/∂xi)u(xi)	Degrees of Freedom (ν_i)	Type	Source of Data
P_{method}	Precision for the entire method	19.92	ug/g	0.01	ug/g	1	0.0144	39	A	Replicate analysis of the 4 ampoules
R_{sample}	Measurement of Rsample	0.92		Covered within P_{method}		-	-	-	-	-
$R_{standard}$	Measurement of Rstd	0.94		Covered within P_{method}		-	-	-	-	-
$M_{Z (L)}$	Balance linearity	0.42	g	0.0003	g	47.417	0.014	Large	B	Balance calibration certificate
C_{calib}		20.1	ug/g	0.05025	ug/g	0.991	0.0498	Large	B	Supplier's specification
$M_{Ysmp (L)}$	Balance linearity	0.2	g	0.0003	g	99.575	0.0299	Large	B	Balance calibration certificate
$M_{Ystd (L)}$	Balance linearity	0.2	g	0.0003	g	-99.575	-0.0299	Large	B	Balance calibration certificate
$M_{X (L)}$	Balance linearity	0.44	g	0.0003	g	-45.262	-0.0136	Large	B	Balance calibration certificate

uc= 0.07

NMIJ: *p*-xylene

Parameter	Source of Uncertainty	X_i		$U(x_i)$		(∂f/∂xi)	(∂f/∂xi)u(xi)	Degrees of Freedom (ν_i)	Type	Source of Data
P_{method}	Precision for the entire method	28.12	ug/g	0.02	ug/g	1	0.0192	39	A	Replicate analysis of the 4 ampoules
R_{sample}	Measurement of Rsample	0.97		Covered within P_{method}		-	-	-	-	-
$R_{standard}$	Measurement of Rstd	1		Covered within P_{method}		-	-	-	-	-
$M_{Z (L)}$	Balance linearity	0.42	g	0.0003	g	66.959	0.020	Large	B	Balance calibration certificate
C_{calib}		28.4	ug/g	0.071	ug/g	0.990	0.0703	Large	B	Supplier's specification
$M_{Ysmp (L)}$	Balance linearity	0.2	g	0.0003	g	140.614	0.0422	Large	B	Balance calibration certificate
$M_{Ystd (L)}$	Balance linearity	0.2	g	0.0003	g	-140.614	-0.0422	Large	B	Balance calibration certificate
$M_{X (L)}$	Balance linearity	0.44	g	0.0003	g	-63.915	-0.0192	Large	B	Balance calibration certificate

uc= 0.10

VSL

The content of each ampoule is divided in two aliquotes and placed in an autosampler vial and added of internal standard.

2 series of measurements are carried out (samples + gravimetrically prepared liquid calibrants (BTEX in MeOH))

A weighted line of regression is obtained for each component in each series.

The component average result per series (4 samples analysed twice) and corresponding uncertainty are further calculated

The contributions to the standard uncertainty of each series (U (k=2) between 1-5%) are mainly:

a- calibrants preparation (weighing, purity and potential losses due to evaporation)
b- lack of fit and regression coefficient uncertainties (main uncertainty source)
c- repeatability of the sample measurement

The final value is the mean value of the two series of measurements.

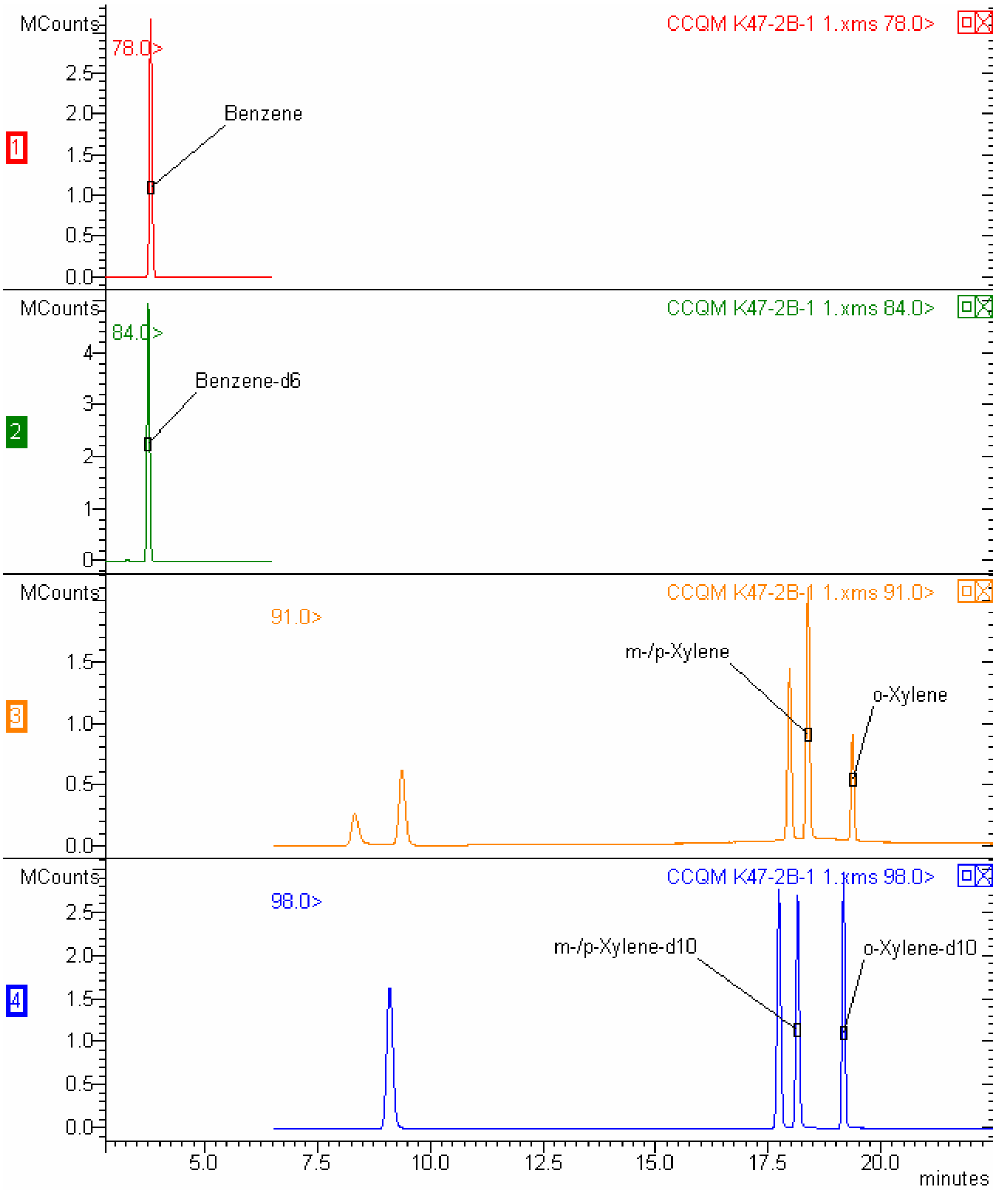
The uncertainty in the final result is the pooled estimate of uncertainty of the series of measurements added of the mean standard deviation of the two series results.

The reported expanded standard uncertainty has a coverage factor of two.

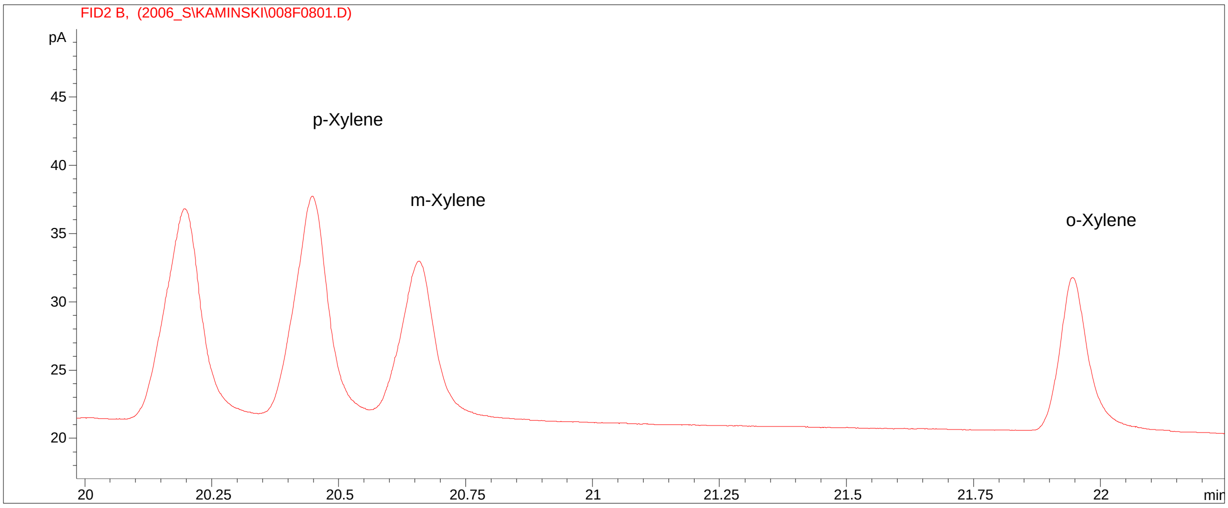
APPENDIX B: Chromatograms

BAM

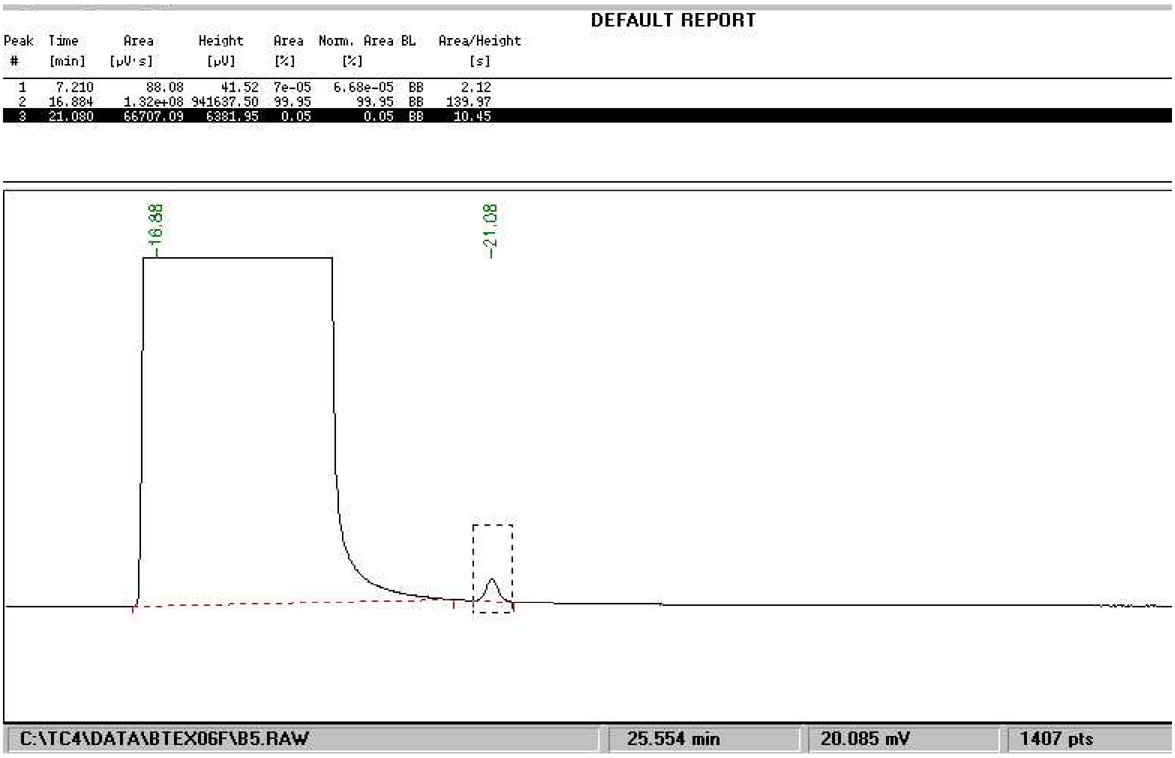
GC-MS, K47 sample



GC-FID K47 sample

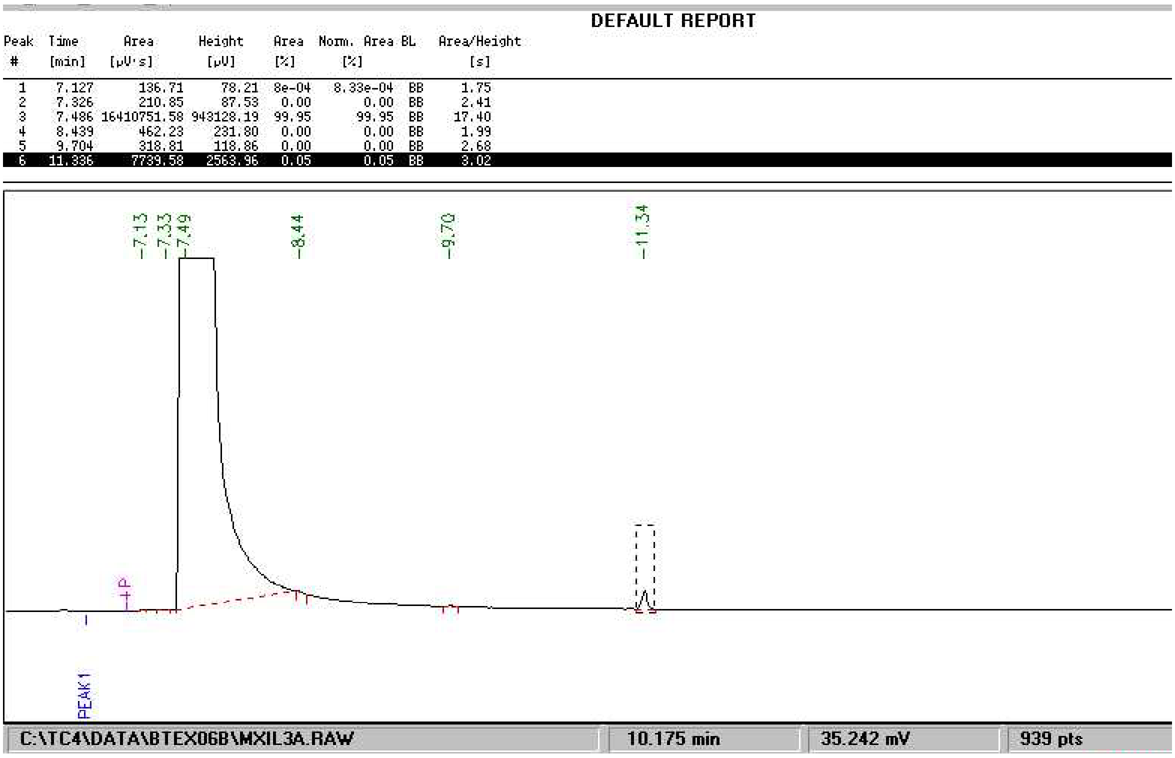


CENAM


DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.210	88.08	41.52	7e-05	6.68e-05	BB	2.12
2	16.884	1.32e+08	941637.50	99.95	99.95	BB	139.97
3	21.080	66707.09	6381.95	0.05	0.05	BB	10.45

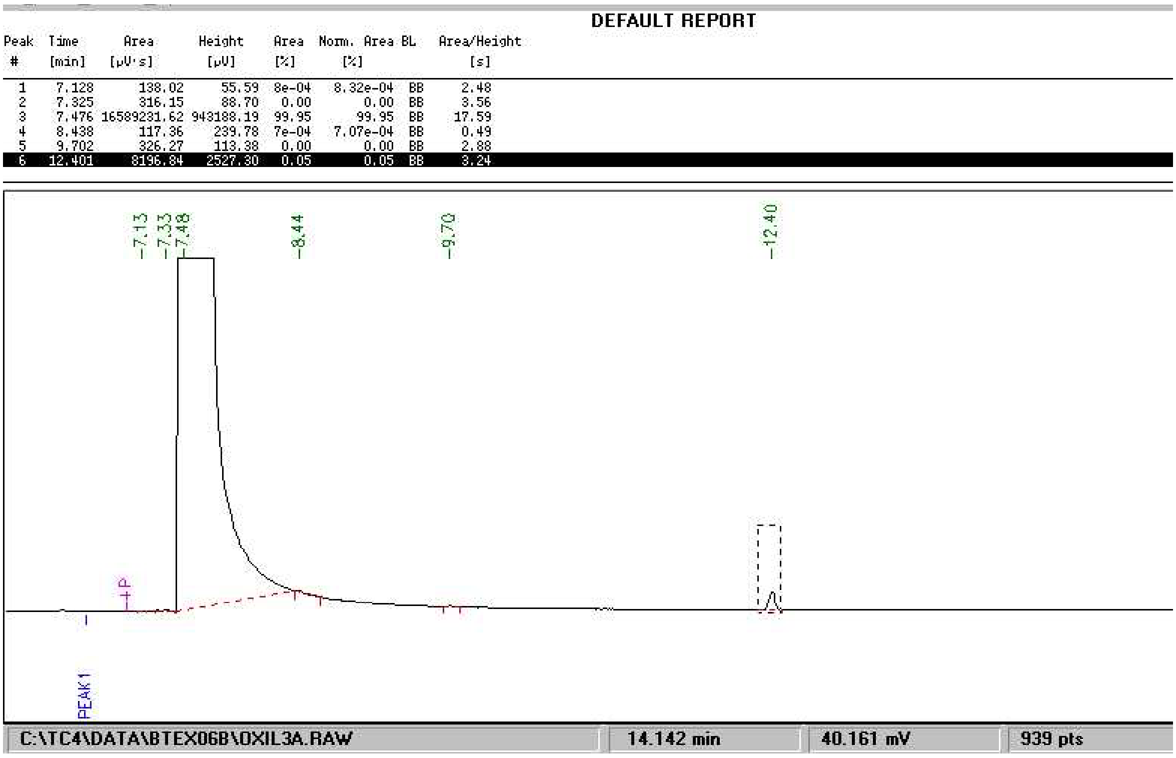
C:\TC4\DATA\BTEX06F\B5.RAW | 25.554 min | 20.085 mV | 1407 pts



```
                                                                          DEFAULT REPORT
Peak  Time      Area        Height     Area  Norm. Area BL    Area/Height
 #    [min]   [µV·s]        [µV]       [%]      [%]                 [s]

  1   7.127       136.71       78.21  8e-04   8.33e-04  BB         1.75
  2   7.326       210.85       87.53  0.00        0.00  BB         2.41
  3   7.486  16410751.58  943128.19  99.95       99.95  BB        17.40
  4   8.439       462.23      231.80  0.00        0.00  BB         1.99
  5   9.704       318.81      118.86  0.00        0.00  BB         2.68
  6  11.336      7739.58     2563.96  0.05        0.05  BB         3.02
```

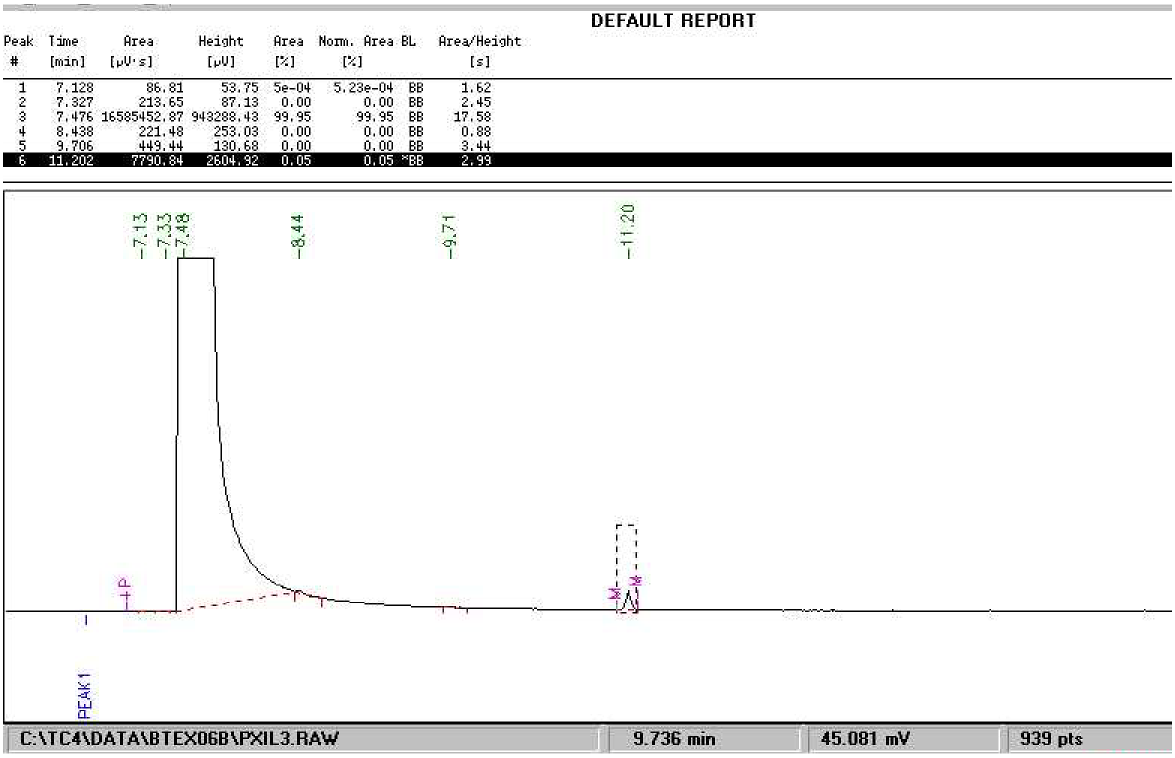
```
C:\TC4\DATA\BTEX06B\MXIL3A.RAW    10.175 min    35.242 mV    939 pts
```



```
                                                                          DEFAULT REPORT
Peak  Time      Area        Height     Area  Norm. Area BL    Area/Height
 #    [min]   [µV·s]        [µV]       [%]      [%]                 [s]

  1   7.128       138.02       55.59  8e-04   8.32e-04  BB         2.48
  2   7.325       316.15       88.70  0.00        0.00  BB         3.56
  3   7.476  16589231.62  943188.19  99.95       99.95  BB        17.59
  4   8.438       117.36      239.78  7e-04   7.07e-04  BB         0.49
  5   9.702       326.27      113.38  0.00        0.00  BB         2.88
  6  12.401      8196.84     2527.30  0.05        0.05  BB         3.24
```

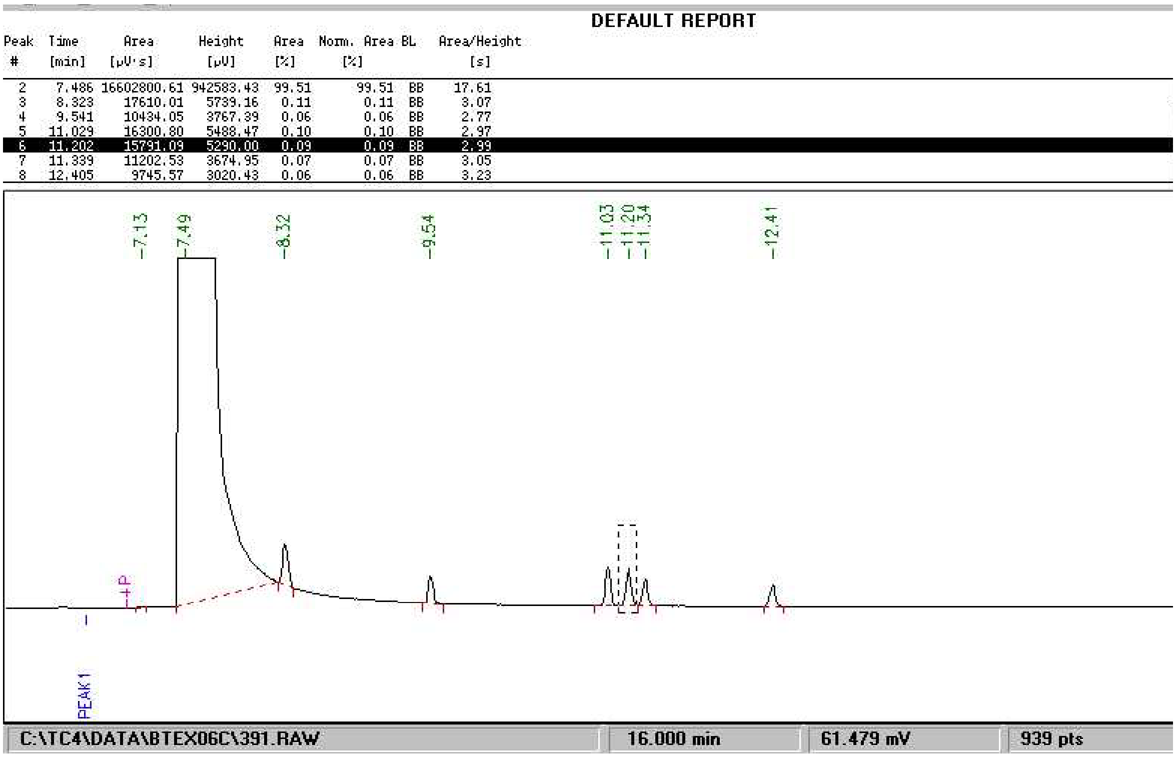
```
C:\TC4\DATA\BTEX06B\OXIL3A.RAW    14.142 min    40.161 mV    939 pts
```



```
                                                                        DEFAULT REPORT
Peak  Time      Area        Height    Area  Norm. Area BL   Area/Height
 #    [min]   [µV·s]        [µV]      [%]       [%]              [s]

  1    7.128       86.81      53.75  5e-04   5.23e-04  BB      1.62
  2    7.327      213.65      87.13   0.00       0.00  BB      2.45
  3    7.476 16585452.87  943288.43  99.95      99.95  BB     17.58
  4    8.438      221.48     253.03   0.00       0.00  BB      0.88
  5    9.706      449.44     130.68   0.00       0.00  BB      3.44
  6   11.202     7790.84    2604.92   0.05       0.05 *BB      2.99
```

C:\TC4\DATA\BTEX06B\PXIL3.RAW | 9.736 min | 45.081 mV | 939 pts

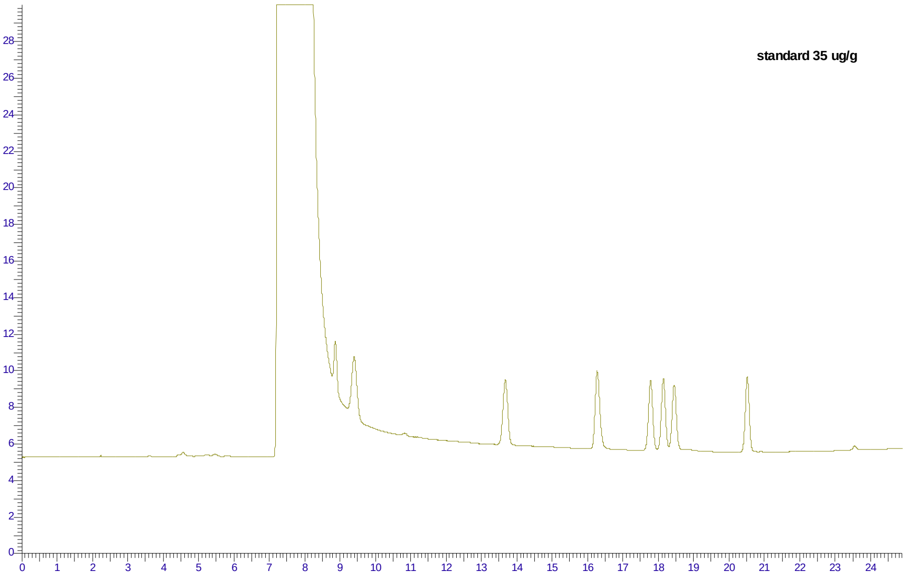


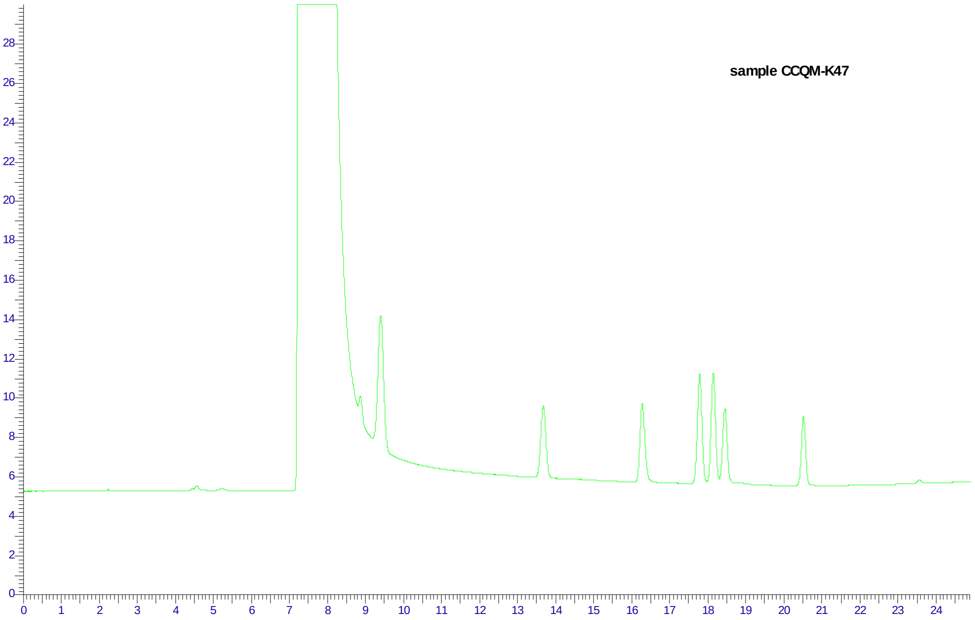
```
                                                                        DEFAULT REPORT
Peak  Time      Area        Height    Area  Norm. Area BL   Area/Height
 #    [min]   [µV·s]        [µV]      [%]       [%]              [s]

  2    7.486 16602800.61  942583.43  99.51      99.51  BB     17.61
  3    8.323    17610.01    5739.16   0.11       0.11  BB      3.07
  4    9.541    10434.05    3767.39   0.06       0.06  BB      2.77
  5   11.029    16300.80    5488.47   0.10       0.10  BB      2.97
  6   11.202    15791.09    5290.00   0.09       0.09  BB      2.99
  7   11.339    11202.53    3674.95   0.07       0.07  BB      3.05
  8   12.405     9745.57    3020.43   0.06       0.06  BB      3.23
```

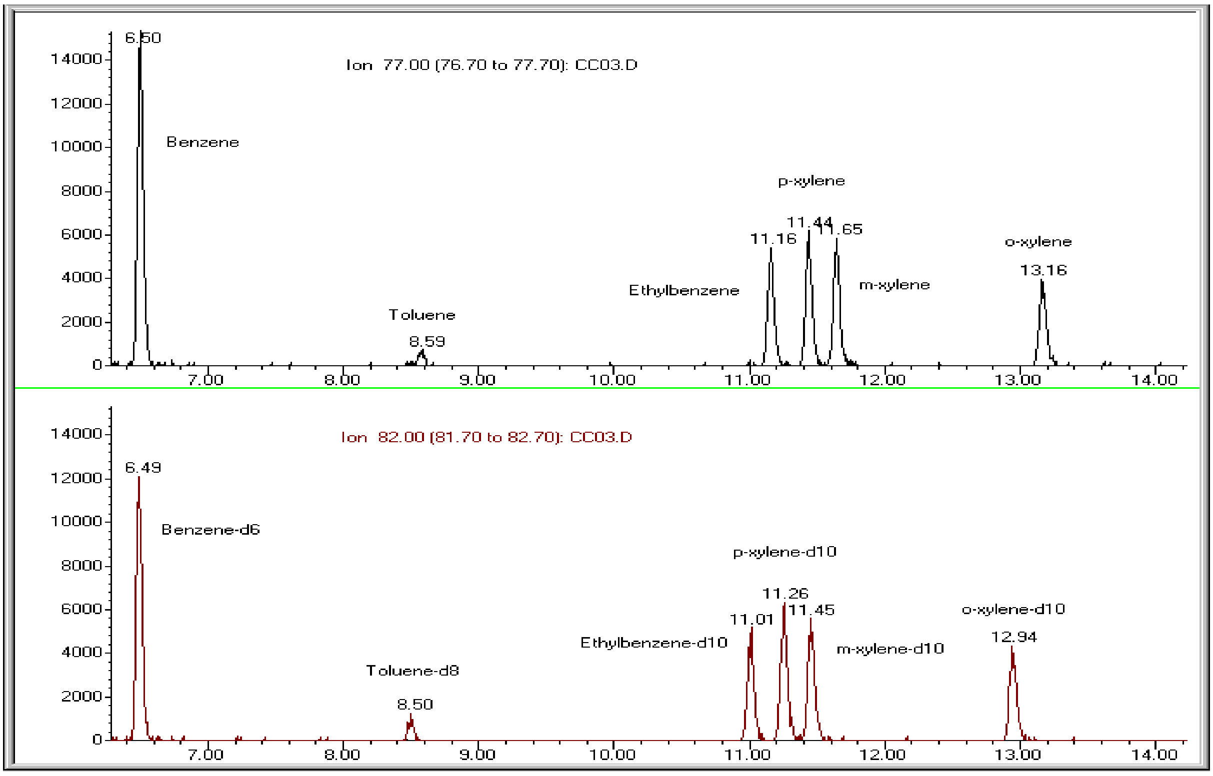
C:\TC4\DATA\BTEX06C\391.RAW | 16.000 min | 61.479 mV | 939 pts

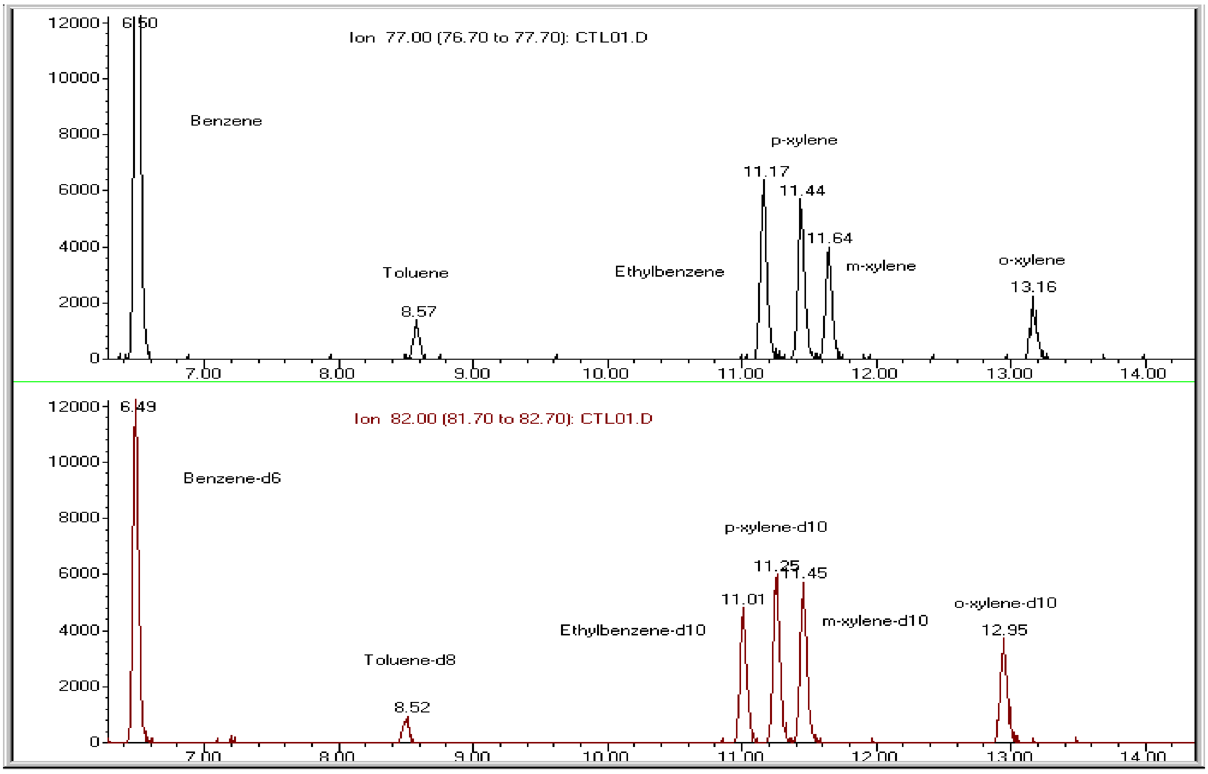
INTI


standard 35 ug/g
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24


sample CCQM-K47
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

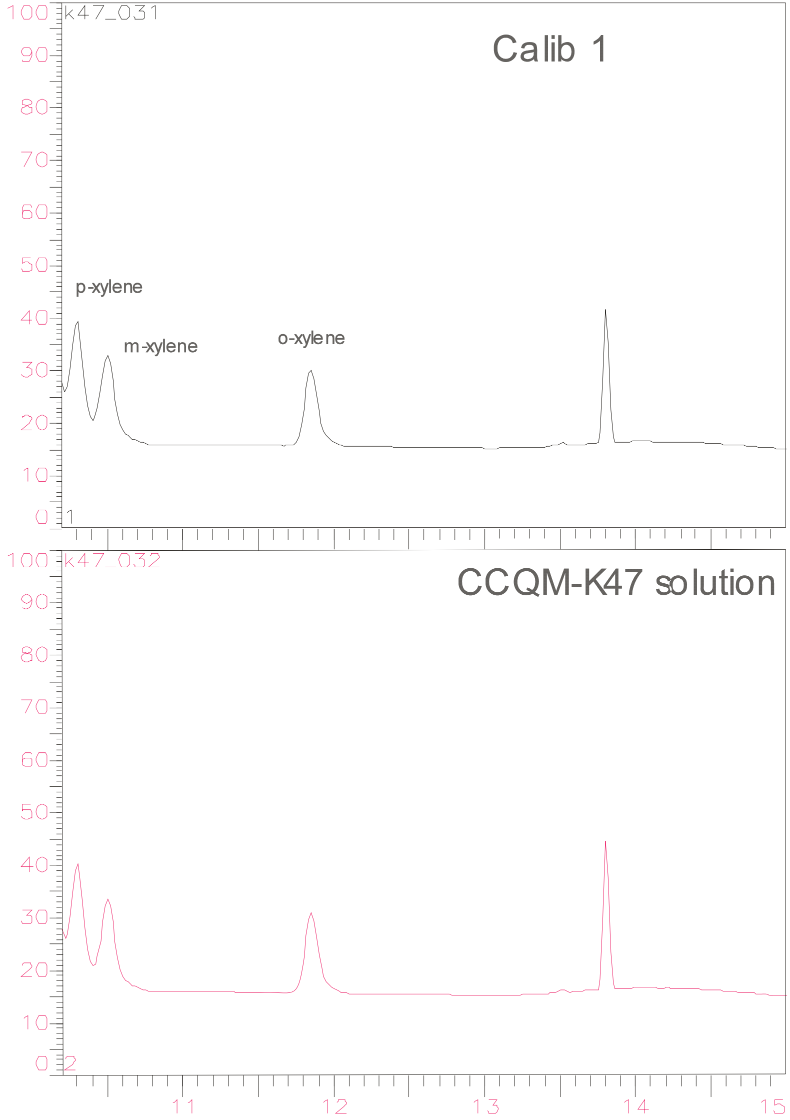
KRISS


Ion 77.00 (76.70 to 77.70): CC03.D
14000
12000
10000
8000
6000
4000
2000
0
6.50
Benzene
Toluene
8.59
Ethylbenzene
11.16
p-xylene
11.44
11.65
m-xylene
o-xylene
13.16
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
Ion 82.00 (81.70 to 82.70): CC03.D
6.49
Benzene-d6
Toluene-d8
8.50
Ethylbenzene-d10
11.01
p-xylene-d10
11.26
11.45
m-xylene-d10
o-xylene-d10
12.94


Ion 77.00 (76.70 to 77.70): CTL01.D
12000
10000
8000
6000
4000
2000
0
6.50
Benzene
Toluene
8.57
Ethylbenzene
11.17
p-xylene
11.44
11.64
m-xylene
o-xylene
13.16
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
Ion 82.00 (81.70 to 82.70): CTL01.D
6.49
Benzene-d6
Toluene-d8
8.52
Ethylbenzene-d10
11.01
p-xylene-d10
11.25
11.45
m-xylene-d10
o-xylene-d10
12.95

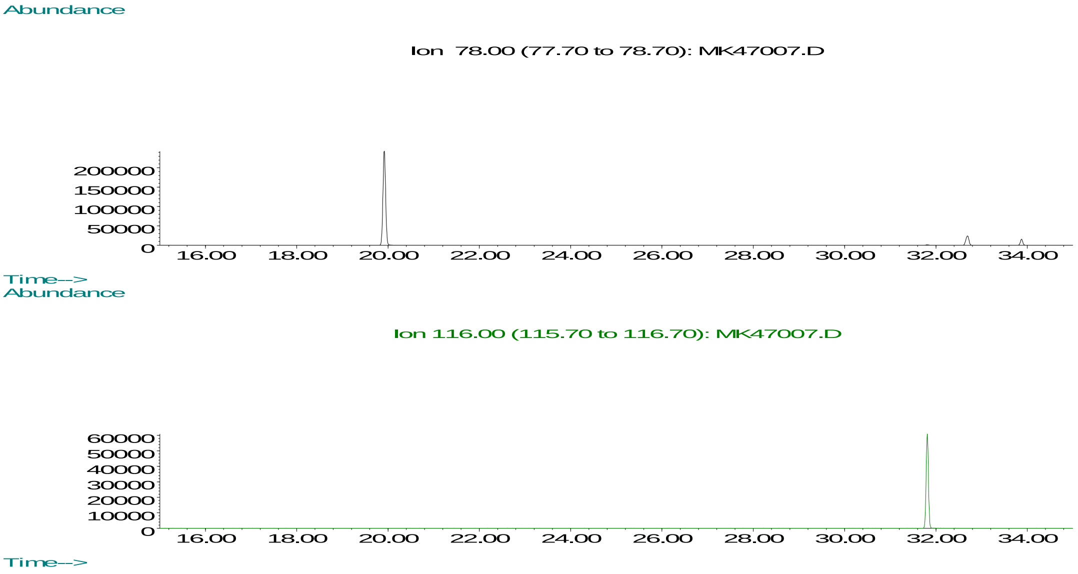
NIST

GC-FID for Xylenes

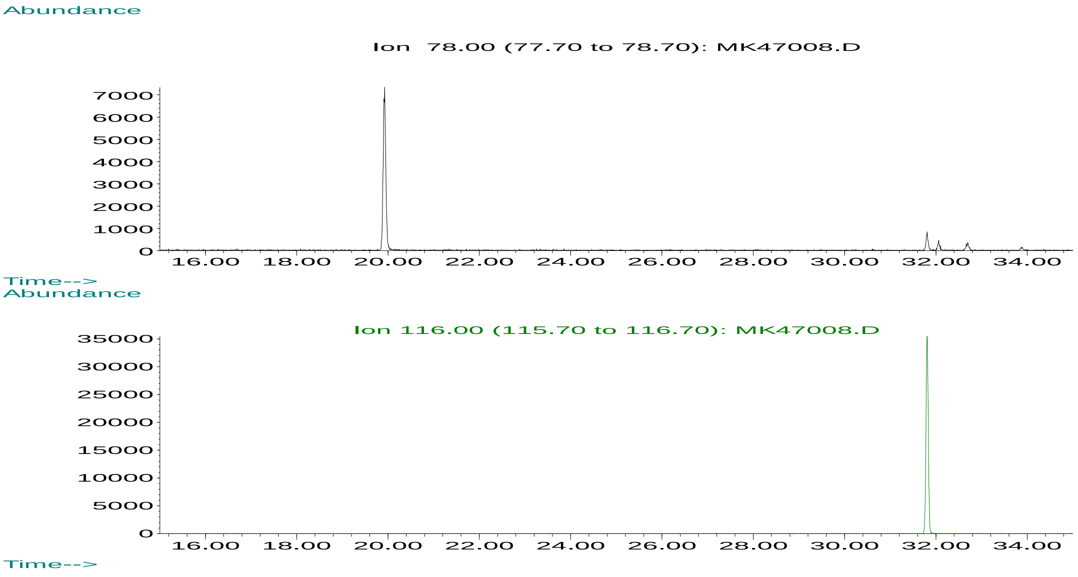


NMIJ

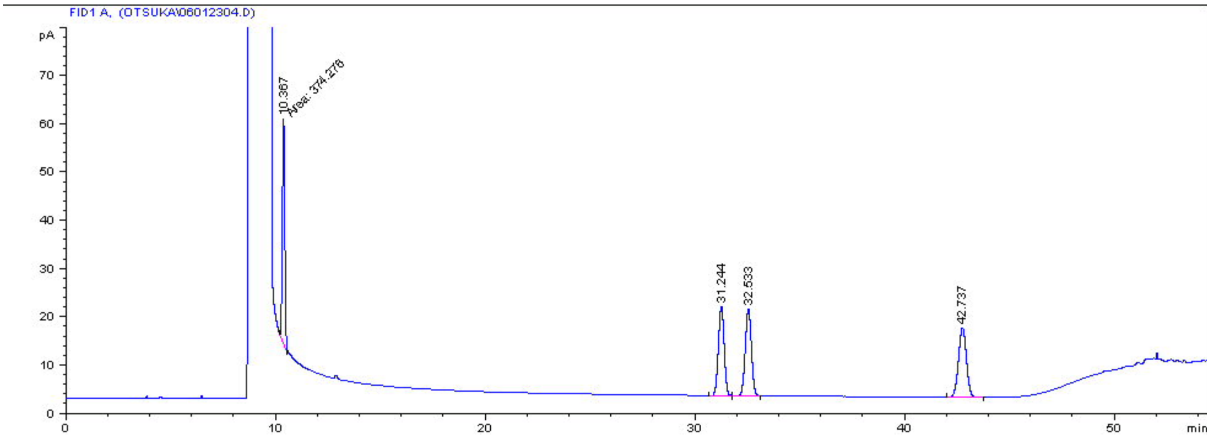
GC/MS for Benzene – Calibration Solution

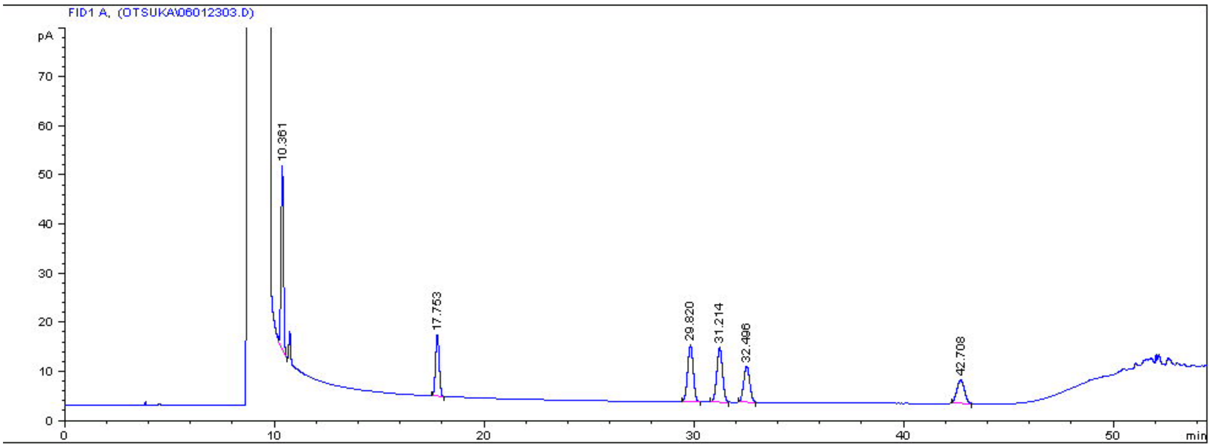


GC/MS for Benzene – CCQM-K47 Solution



VSL


FID1 A, (OTSUKA\06012304.D)
pA
70
60
50
40
30
20
10
0
10.367
Area: 374.278
31.244
32.533
42.737
0
10
20
30
40
50
min


FID1 A, (OTSUKA\06012303.D)
pA
70
60
50
40
30
20
10
0
10.361
17.753
29.820
31.214
32.496
42.708
0
10
20
30
40
50
min