Final Report

DETERMINATION of PLASTICIZERS

Method development, validation and peer review for
CEN TC 52 WG9 TG2
Safety of toys – Organic chemical compounds –
Methods of analysis
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by

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General study data

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Laboratory work

Chemcon GmbH
Zirkusgasse 23
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Time schedule

November 2001 - January 2003

Contract

LGC (Teddington) Limited
Agreement LGC/GC20/ON1

Context

European Commission
Order Voucher BC/CEN/03/229/970-29
relating to Mandate M/229
„Organic chemical compounds in toys other than chemical toys“

Monitoring

Members of CEN TC 52 WG9 TG2
Organic chemical compounds – Methods of analysis

Contents

1 Introduction

This report describes the development of a method for the determination of 21 plasticizers from an aqueous solution including validation and Peer Review. The work has been carried out in the framework of the development of European standards dealing with organic chemicals in toys within the European Committee of Standardisation (CEN).

The migration of the plasticizers contained in toys into water by shaking a toy sample in water is described in the European draft standard prEN 71-10: “Organic chemical compounds – Sample preparation and extraction”, and is outside the scope of this report. The thought starting point for the work was the aqueous solution obtained from the extraction of a toy sample.

Document CEN TC 52 WG9 TG2 N94 rev4 corr1 (February 2002) contained two lists of plasticizers requiring methods of analysis as a first and a second priority. The first priority substances were meant to be included in the first edition of the standard. The second list was intended to be added at a later stage. However, it was understood that the lead laboratory should cover, if possible without major difficulties, also as many as possible substances from the second list.

NOTE: Due to difficulties encountered in the toxicological assessment of many plasticizers and in view of the request of the Commission to include only substances classified dangerous according to Council Directive 67/548/EEC a number of first priority plasticizers has been later moved to the second priority list. Only triphenyl phosphate and the o-, m- and p-isomers of tritolyl (tricresyl) phosphate have been retained as a first priority (see document CEN TC 52 WG9 TG2 N139 rev1 (May 2002)).

All 11 plasticizers contained in the first priority list of document CEN TC 52 WG9 TG2 N94 rev4 corr1 have been included in this study and 9 out of 18 plasticizers from the second priority list. However, one of the substances – didecyl adipate – contained in the second priority list had to be removed. It turned out that the delivered standard was not didecyl adipate. The selection was based in part on practical considerations (availability of standards) and in part on toxicological relevance.

In addition, we added bis(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP) despite the fact that these plasticizers will not be included in the standard. It was considered useful to incorporate these two phthalates for comparison purposes and to ensure that the method works for all relevant groups of plasticizers (to avoid that two different methods need to be applied). Another important reason was to ensure that those two widely used phthalates do not adversely affect the analysis of the other plasticizers.

The limit values have been determined in the following way: In accordance with CEN TC 52 WG9 TG3 N197 rev2 "Final opinion of TG3 regarding plasticizers in Toys" 10% of the TDI value has been chosen in those cases where a TDI value has been established by SCF (bis(2-ethylhexyl) adipate

and butyl benzoate). For the phthalates the same approach was chosen taking 10% of the TDIs set by CSTEE.

As the TDI value for triethyl citrate set by JECFA is extremely high - 20 mg/kg body weight (which is a factor of ~130 higher than the TDI for DINP) - it does not seem to make a lot of sense to set a limit for this substance in toys (assuming that the migration behaviour of citrates is of the same order of magnitude than the one of phthalates). However, the substance is a sensitiser in animals. If sensitising properties for humans could be shown the limit would presumably considerably lower. For this reason we included triethyl citrate but used the SCF group restriction value of 0,05 mg/kg body weight (which SCF did not set for this substance).

For both dibenzoates the NOEL mentioned in CEN TC 52 WG9 TG3 N188 "A hazard based prioritisation scheme for plasticizers in toys" (by Suzi Cotrell) was used (500 mg/kg/d). From this NOEL a TDI was derived by applying a safety factor of 100 (5 mg/kg/d). A tenth of this value was used.

In all other cases the group restriction value of the SCF was used in case it was set. The same value of 0,05 mg/kg/d was also used for triethyl *o*-acetylcitrate,
bis[2-(2-butoxyethoxy)ethyl] adipate and bis(2-butoxyethyl) adipate for which no group restriction limit was defined.

The other assumptions were:
10 kg child
3 hours sucking (time for shaking of toy sample only 1 hour!)
10 cm² sucking area
100 ml (2x50ml) water for extraction

Example: bis(2-ethylhexyl) adipate
TDI: 300 µg/kg/d, 10% = 30 µg/kg/d
=> 10 kg child: 300 µg/child/d
assumption: child sucks 3 hours
=> in 1 hour only a third of this amount must be released: 100 µg
The maximum amount which may be found in 100 ml water after extraction of 10 cm² toy sample is 100 µg bis(2-ethylhexyl) adipate.

For triphenyl phosphate and the tritolyl (tricresyl) phosphate isomers the lead laboratory was requested to determine the limit of detection and the limit of quantitation, respectively.

List of plasticizers covered by this study including target concentrations:

Substance	**CAS Number**	**in 100ml H_2O**
Tributyl citrate	77-94-1	170µg
Tributyl *O*-acetyl citrate	77-90-7	170µg
Triethyl citrate	77-93-0	170µg
Triethyl *O*-acetylcitrate	77-89-4	170µg
Bis(2-ethylhexyl) adipate	103-23-1	100µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	170µg
Bis(2-butoxyethyl) adipate	141-18-4	170µg
Dioctyl adipate	123-79-5	170µg
Didecyl adipate*	105-97-5	170µg
Diisodecyl adipate	27178-16-1	170µg
Bis(2-ethylhexyl) azelate	103-24-2	170µg
Bis(2-ethylhexyl) sebacate	122-62-3	170µg
Butyl benzoate	136-60-7	1700µg as benzoic acid
Di(ethylene glycol) dibenzoate	120-55-8	1700µg
Di(propylene glycol) dibenzoate	94-51-9	1700µg
Tributyl phosphate	126-73-8	170µg
Triphenyl phosphate	115-86-6	ND (~1µg)**
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	ND (~1µg)**
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	ND (~1µg)**
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	ND (~1µg)**
Bis(2-ethylhexyl) phthalate	117-81-7	12µg
Diisononyl phthalate	68515-48-0	50µg

* Didecyl adipate was initially included, but eliminated later (see text)

** ND=Not detectable, to be determined by lead laboratory, estimated to be about 1µg

2 Experimental

2.1 Basic considerations

The analysis of organic substances in water with GC/MS requires sample treatment for changing the aqueous solvent to an organic one and to enrich the analytes. In the case of high boiling organic substances like plasticizers 2 options are available: a liquid/liquid or a solid phase extraction.

Both approaches have their pros and cons. An advantage of the liquid/liquid extraction is the use of low cost apparatus and the possibility to be performed by low skilled staff. The possibility of automation of the enrichment step and the use of very small amounts of organic solvent are advantages of the solid phase extraction. However, the operation may require more skills depending on the apparatus used.

A disadvantage of the liquid/liquid extraction is the contamination of the water sample with organic solvent. The used sample has to be treated as hazardous waste. Disadvantages of the solid phase extraction are that they are more cost intensive and that commercially available solid phase extraction cartridges are sometimes contaminated with plasticizers.

Bearing in mind in particular the last point the decision was to give preference to liquid/liquid extraction.

2.2 Apparatus

Gaschromatograph: HP5890 Series II

Analytical column: Optima delta-3 (manufacturer: Macherey & Nagel, Germany), dimensions: 30m*0,25mm*0,25µm

Autoinjector: HP7673A equipped with a 10µl syringe fast injection mode
Split/Splitless-injector at constant pressure, split flow 10ml/min, split injection
Injection volume: 1µl
Pressure: 150kPa Helium (purity 99,999% or better)
Septum purge flow: 2ml/min

Inlet temp.: 275°C
Oven temp. progr.: Init Temp.: 100°C
Init Time: 1min
Rate: 7°C/min
Final Temp.: 300°C
Final Time: 10min
Transfer-Line Temp.: 290°C

Mass selective Detector: HP5970B

Software: G1701AA Rel. A03.00

Single Ion monitoring: For each substance two ions were used for quantification: typically the base ion as target ion and the ion showing the second highest peak in the mass spectrum as qualifier. In the case of interference with other substances ions with the next lower peak height were chosen. The target ion is used for quantification, the qualifying ion is used for positive identification of the substance. The use of a qualifier ion reduces the risk of false positive results due to interfering signals. A deviation of 20% from the expected response of the qualifier ion was accepted.

List of target and qualifier ions for plasticizers:

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Tributyl citrate	77-94-1	129	185
Tributyl *O*-acetylcitrate	77-90-7	185	129
Triethyl citrate	77-93-0	157	115
Triethyl *O*-acetylcitrate	77-89-4	157	203
Bis(2-ethylhexyl) adipate	103-23-1	129	111
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	99	85
Bis(2-butoxyethyl) adipate	141-18-4	85	111
Dioctyl adipate	123-79-5	129	241
Diisodecyl adipate	27178-16-1	129	111
Bis(2-ethylhexyl) azelate	103-24-2	171	112
Bis(2-ethylhexyl) sebacate	122-62-3	185	112
Butyl benzoate	136-60-7	105	123
Di(ethylene glycol) dibenzoate	120-55-8	105	149
Di(propylene glycol) dibenzoate	94-51-9	105	163
Tributyl phosphate	126-73-8	99	155
Triphenyl phosphate	115-86-6	325	169
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	165	179
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	368	165
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	368	165
Bis (2-ethylhexyl) phthalate	117-81-7	149	167
Diisononyl phthalate	68515-48-0	149	293

List of target and qualifier ions for internal standard:

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Benzylbutyl phthalate	85-68-7	149	206

Time windows:

Due to interferences two runs using different time windows were required. The first run - program A - covers the internal standard (benzylbutyl phthalate) and all substances except the ones mentioned below for the second run. The second run - program B - covers the internal standard, bis (2-ethylhexyl) phthalate, triphenyl phosphate, tri-*o*-tolyl phosphate, tri-*m*-tolyl phosphate and tri-*p*-tolyl phosphate.

Time windows of monitored ions (Program A):

Start time [min]	Monitored ions [amu]
8	99, 105, 115, 123, 155, 157, 203
24	85, 111, 129, 149, 185
29,3	105, 129, 149, 241
31	85, 99, 111, 112, 129, 149, 171, 293

Time windows of monitored ions (Program B):

Start time [min]	Monitored ions [amu]
27	149, 206
29	149, 167, 325, 169
31	165, 179, 368

2.3 Reagents

2.3.1 Chemicals

Methanol, pesticide grade, Code P5513, Labscan Ltd., Ireland

Acetone, pesticide grade, Code P5501, Labscan Ltd., Ireland

Toluene, pesticide grade, Code P5518, Labscan Ltd., Ireland

Cyclohexane, HPLC grade, Code C2508, Labscan Ltd., Ireland

n-Hexane, picograde, Code 1244, Promochem, Germany

n-Heptane, analytical grade, 104379, Merck, Germany

Ethylacetate for pesticide residue analysis, Code 3427, Promochem, Germany

Sodiumchloride (NaCl), 6404, Merck, Germany

Disodiumhydrogenphosphate Decahydrate ($Na_2HPO_4.12H_2O$), 6579, Merck, Germany

Phosphoric acid 85%, analytical grade, 100573, Merck, Germany

Magnesiumsulfate Heptahydrate ($MgSO_4.7H_2O$), 105886, Merck, Germany

Benzylbutyl phthalate 98%, 30,850-1, Sigma-Aldrich, Austria

2.3.2 Plasticizers

Name	Purity according to manuf.	CAS-Nr.	Manufacturer	Order-Nr.	Ch.Nr.
Tributyl citrate	>99%	77-94-1	Merck	8.203.500.100	S23527 102
Tributyl O-acetyl citrate	>99.0%	77-90-7	Fluka	42858	415938/1 20502
Triethyl citrate	>98%	77-93-0	Fluka	27500	423804/1 32201
Triethyl O-acetyl citrate	>99.0%	77-89-4	Fluka	68536	416283/1 13801
Bis(2-ethylhexyl) adipate	>99%	103-23-1	Fluka	WA17455	308606/1 53900
Bis[2-(2-butoxyethoxy)ethyl] adipate	?	141-17-3	Aldrich	42,101-4	11901PU
Bis(2-butoxyethyl) adipate	Techn.	141-18-4	Aldrich	46,023-0	05224HQ
Dioctyl adipate	?	123-79-5	Chem Service	Pz-325	55-121L
Dicapryl adipate	?	?	Chem Service	2750B	55-79N
Diisodecyl adipate	Techn.	27178-16-1	Aldrich	46,021-4	04224HQ
Bis(2-ethylhexyl) azelate	Ca. 80%	103-24-2	Merck	8.013.170.100	S25705 005
Bis(2-ethylhexyl) sebacate	>97%	122-62-3	Fluka	WA12729	48396/1 43901
Butyl benzoate	>98%	136-60-7	Fluka	12410	367947/1 54200
Di(ethylene glycol) dibenzoate	96%	120-55-8	Aldrich	36,936-5	05027ES
Di(propylene glycol) dibenzoate	?	94-51-9	Chem Service	Pz-96	61-55D
Tributyl phosphate	p.A. >99%	126-73-8	Merck	1.083.540.500	K28998154 117
Triphenyl phosphate	>98%	115-86-6	Fluka	93080	361606/1 22301
Tri-*o*-cresyl phosphate	98%	78-30-8	Chem Service	O-918	273-43A
Tri-*m*-tolyl phosphate	97%	563-04-2	Acros	422280100	A010989901
Tri-*p*-tolyl phosphate	>98%	78-32-0	Acros	422300250	A010354501
Bis(2-ethylhexyl) phthalate	> 97%	117-81-7	Fluka	80032	420656/1 40201
Diisononyl phthalate	techn.	68515-48-0	Fluka	80072	24260/1 1295

2.3.3 Purity of plasticizers

The first step in the development of the method of analysis was the characterisation of the delivered chemicals:

Plasticizers were diluted in pesticide grade methanol and analysed by GC/MS. First striking result was that several chemicals seemed to be of low purity containing up to 40% of methylesters.

To verify the suspected impact of methanol the substances were diluted in pesticide grade toluene and again analysed by GC/MS. In this experiment the purity of all chemicals as indicated by the manufacturer could be confirmed.

These results indicate, that the analysed plasticizers undergo a transesterification-reaction with methanol, leading to the conclusion, that in all following experiments short chain alcohols (e.g. methanol, ethanol,…) had to be eliminated.

No supplier for didecyl adipate could be found. However, some information suggested that dicapryl adipate could be a trivial name for this plasticizer. Hence, it was ordered. Dicapryl adipate was analysed and it was found that the data did not comply with the behaviour to be expected: it should elute from apolar analytical columns after dioctyl adipate. In fact, the substance labelled as “dicapryl adipate” elutes earlier, which indicates shorter side chains such as dihexyl adipate. This discrepancy may derive from labelling the substance with a trivial name. Therefore this substance was withdrawn form the list of plasticizers to be analysed.

2.4 Selection of analytical column

According to the chemical nature of the analytes our first choice was a nonpolar analytical column type DB-5 (5%-phenyl-, 95%-methylsilicone), dimensions: 60m*0,25mm*0,25µm, J&W Scientific. On this column the following substances failed to be separated: tri-m-tolyl phosphate and bis(2-ethylhexyl) azelate, bis(2-ethylhexyl) sebacate and bis[2-(2-butoxyethoxy)ethyl] adipate.

Next choice was an analytical column type MS-1 (100% methylsilicone with especially bonded phase), dimensions: 15m*0,25mm*0,25µm, Agilent Technologies. On this column the following substances could not be separated satisfactorily: tributyl phosphate and triethyl citrate, bis(2-ethylhexyl) adipate and di(ethylene glycol) dibenzoate, tri-*o*-cresyl phosphate and di-n-octyl adipate and bis(2-ethylhexyl) phthalate.

The third analytical column tested was an Optima delta-3 (phenyl-methylsilicone with especially bonded phase, Macherey & Nagel, Germany), dimensions: 30m*0,25mm*0,25µm. On this column all substances could be satisfactorily separated with the exception of diisodecyl adipate and diisononyl phthalate, which are not separable due to their large number of isomers. Those substances, which elute near the signal heaps of diisononyl phthalate and diisodecyl adipate were separated mathematically by analysing the single ions

2.5 Environmental and health hazard considerations

The use of a solid phase extraction would have been preferable from an environmental point of view. However, for reasons outlined in 2.1 it was decided to employ a liquid/liquid-extraction method.

In order to minimise environmental and health impacts no halogenated solvents have been applied. Both for economic and environmental reasons one of the aims was to use an amount of solvent as low as possible and to avoid multiple extractions.

Another target was to give preference to the solvent with the higher working place limit (MAK-value) in case of similar extraction efficiency.

3 Results of method development

3.1 Calibration curves

Calibration of the analytical apparatus was performed with dilutions of the plasticizers in pesticide grade toluene. Benzylbutyl phthalate was used as internal standard.

The concentration of the calibration standards were between 0,1µg/ml and 50µg/ml solvent at six to ten levels. The concentration of the internal standard was 5µg/ml.

Due to the great differences in concentrations between the substances (limits reaching from 12µg/100ml H_2O to 1700µg/100ml H_2O) those at the low limits (bis(2-ethylhexyl) phthalate, triphenyl phosphate, tri-*o*-tolyl phosphate, tri-*m*-tolyl phosphate and tri-*p*-tolyl phosphate) have to be analysed in a separate run using different time windows for target and qualifier ions to avoid interferences by the plasticizers present in high concentrations. Example chromatograms are shown in Annex A.

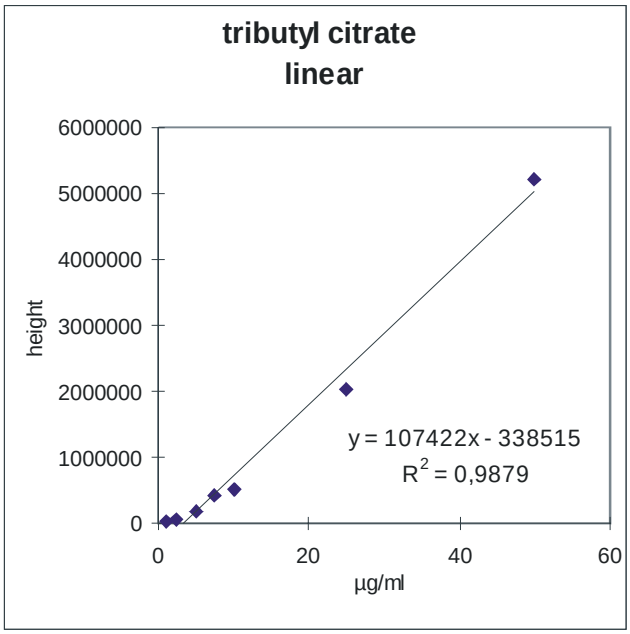
As shown in the table below most of the calibration curves of the analytes were linear with a linear coefficient of correlation > 0,995. For all substances the coefficient of correlation is higher than 0,999 when using a non-linear curve fit (2^{nd} order).

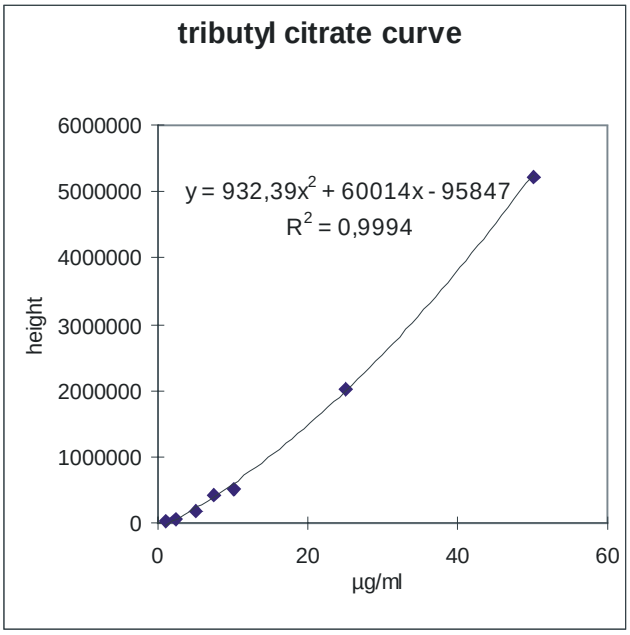
Only one substance tributyl citrate showed a relatively poor coefficient of correlation for a linear curve fit (0,9939). The reason for the non-linear curve fit for tributyl citrate is supposed to be the chemical nature of the substance. The three butoxy-groups opposite the free hydroxyl-group seem to produce a strong dipole effect. This can lead to a certain thermal lability of the substance. Tributyl citrate elutes later from the column than triethyl citrate and must therefore stand a higher thermal stress. Interactions of the free hydroxyl group with the column wall are possible. This effect is only slightly visible for the O-acetyl citrates, indicating that the acetyl group acts as guard group.

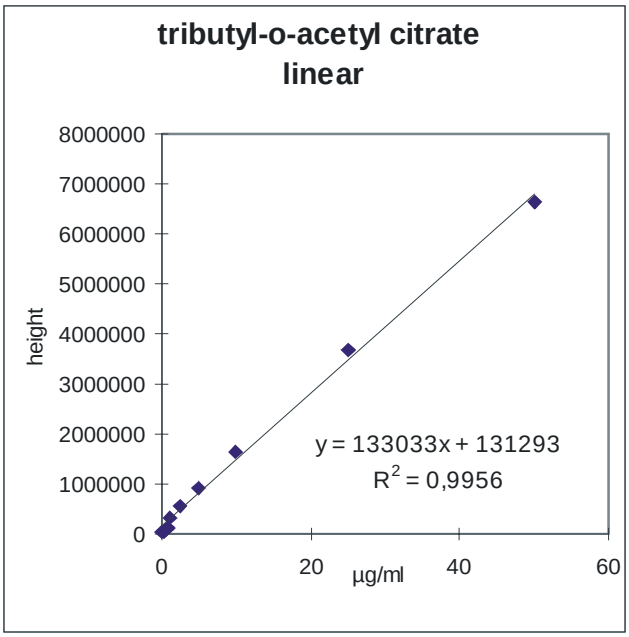
Calibration curves – coefficients of correlation

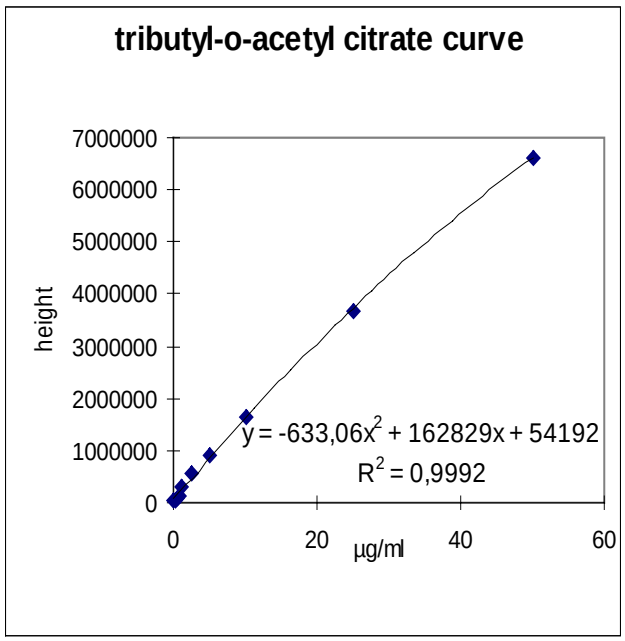
Substance	**Coefficient of correlation (r) linear**	**Coefficient of correlation (r) non-linear**
Tributyl citrate	0,9939	0,9997
Tributyl *O*-acetylcitrate	0,9978	0,9996
Triethyl citrate	0,9996	0,9998
Triethyl *O*-acetylcitrate	0,9992	0,9998
Bis(2-ethylhexyl) adipate	0,9994	0,9998
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,9997	0,9997
Bis(2-butoxyethyl) adipate	0,9996	0,9996
Dioctyl adipate	0,9987	0,9996
Diisodecyl adipate	0,9993	0,9994
Bis(2-ethylhexyl) azelate	0,9987	0,9999
Bis(2-ethylhexyl) sebacate	0,9980	0,9998
Butyl benzoate	0,9994	0,9994
Di(ethylene glycol) dibenzoate	0,9997	0,9997
Di(propylene glycol) dibenzoate	0,9997	0,9998
Tributyl phosphate	0,9999	0,9999
Triphenyl phosphate	0,9980	0,9998
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0,9986	0,9996
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	0,9989	0,9998
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	0,9993	0,9998
Bis (2-ethylhexyl) phthalate	0,9990	0,9995
Diisononyl phthalate	0,9995	0,9996

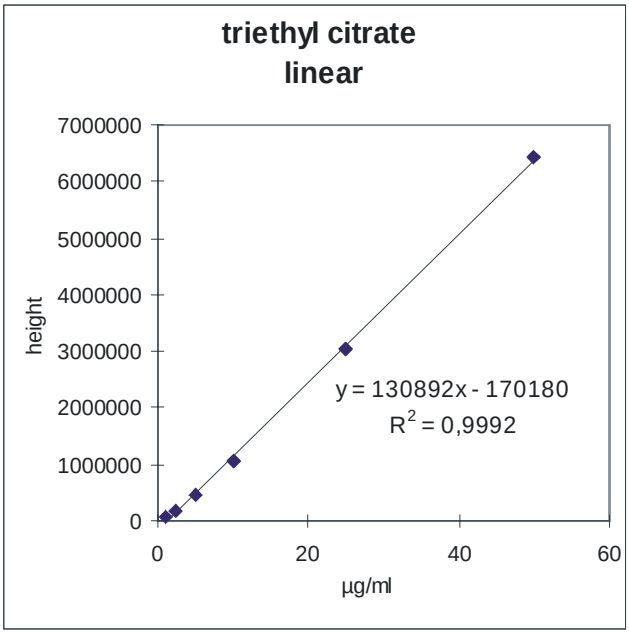
Calibration curves of plasticizers in toluene are shown on the following pages.

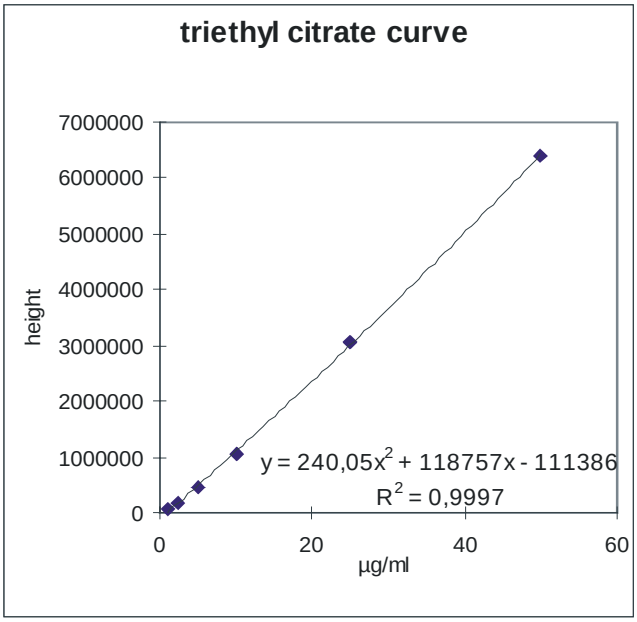

tributyl citrate
linear
height
µg/ml
y = 107422x - 338515
R2 = 0,9879

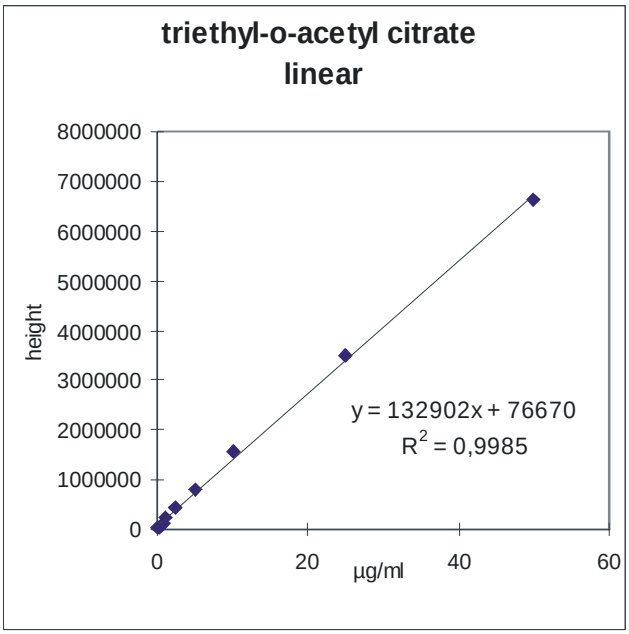

tributyl citrate curve
height
µg/ml
y = 932,39x2 + 60014x - 95847
R2 = 0,9994

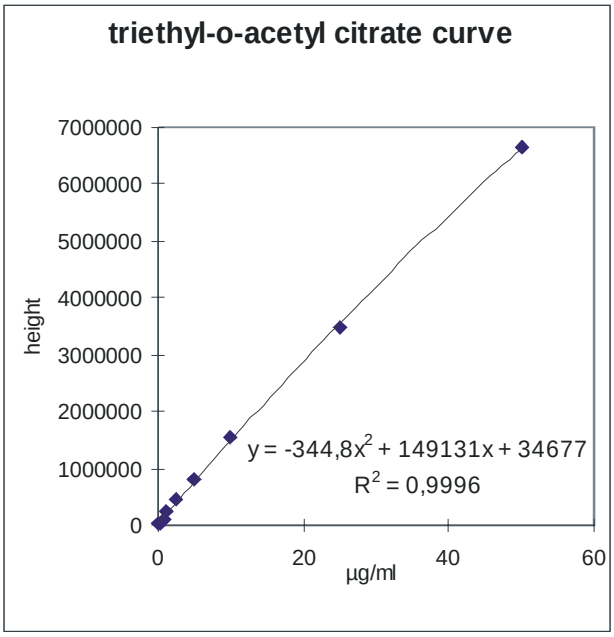

tributyl-o-acetyl citrate
linear
height
µg/ml
y = 133033x + 131293
R2 = 0,9956

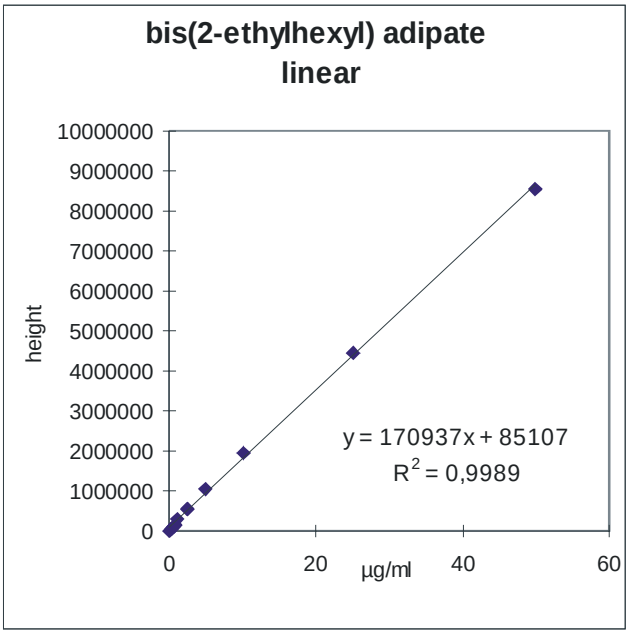

tributyl-o-acetyl citrate curve
height
µg/ml
y = -633,06x2 + 162829x + 54192
R2 = 0,9992

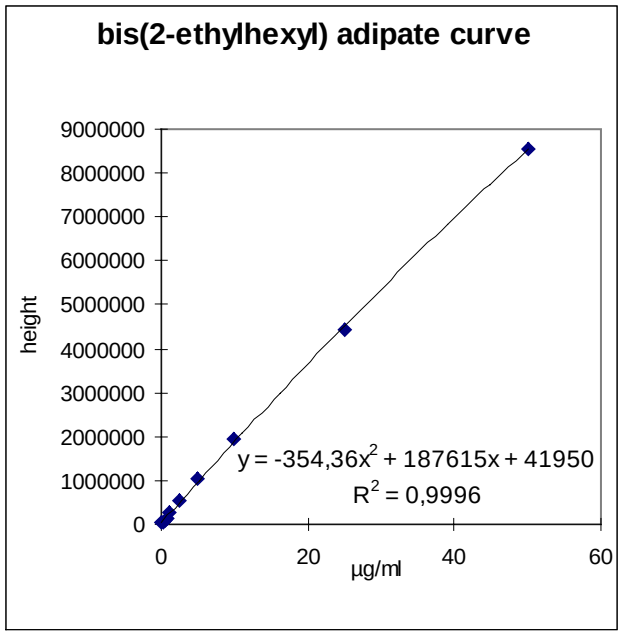

triethyl citrate
linear
height
µg/ml
y = 130892x - 170180
R2 = 0,9992

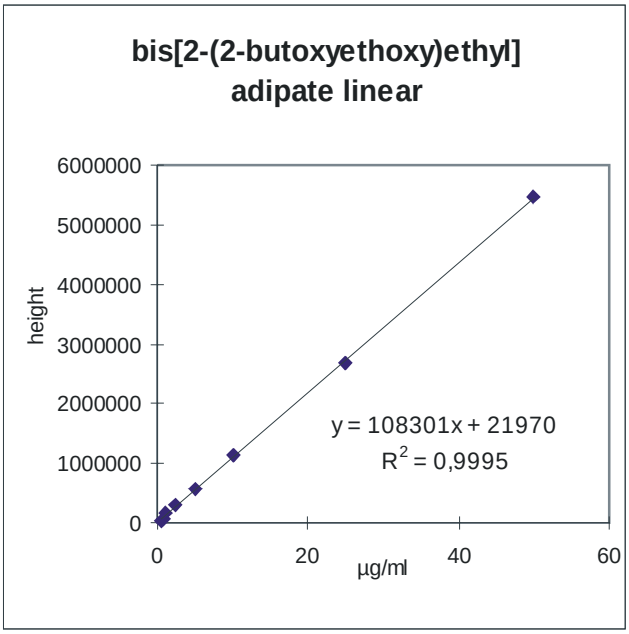

triethyl citrate curve
height
µg/ml
y = 240,05x2 + 118757x - 111386
R2 = 0,9997

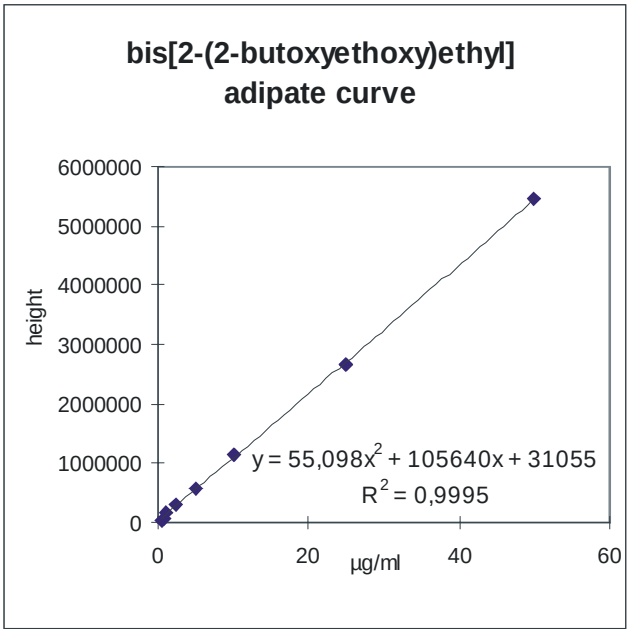

triethyl-o-acetyl citrate
linear
height
µg/ml
y = 132902x + 76670
R2 = 0,9985

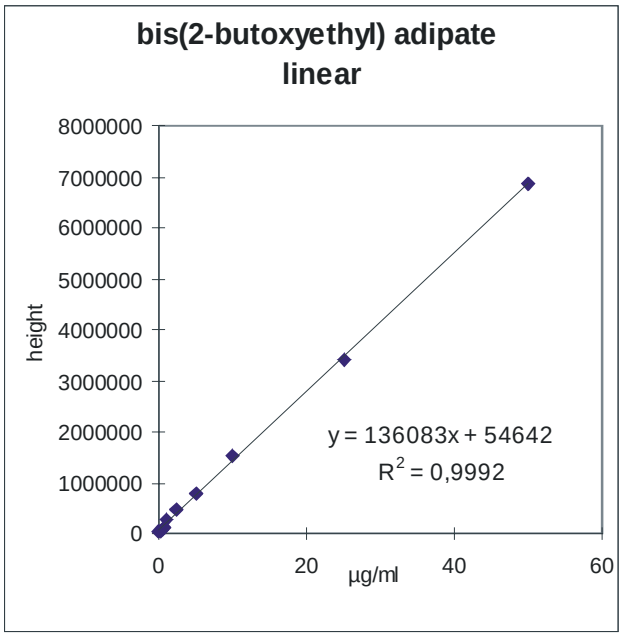

triethyl-o-acetyl citrate curve
height
µg/ml
y = -344,8x2 + 149131x + 34677
R2 = 0,9996

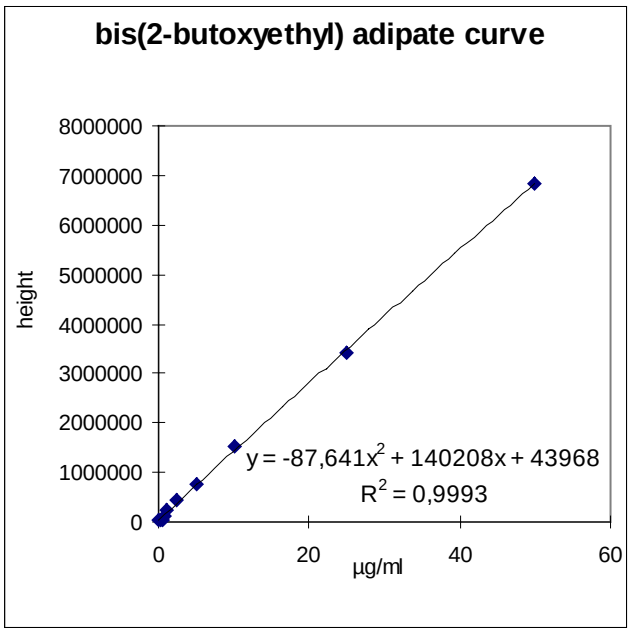

bis(2-ethylhexyl) adipate
linear
height
µg/ml
y = 170937x + 85107
R2 = 0,9989

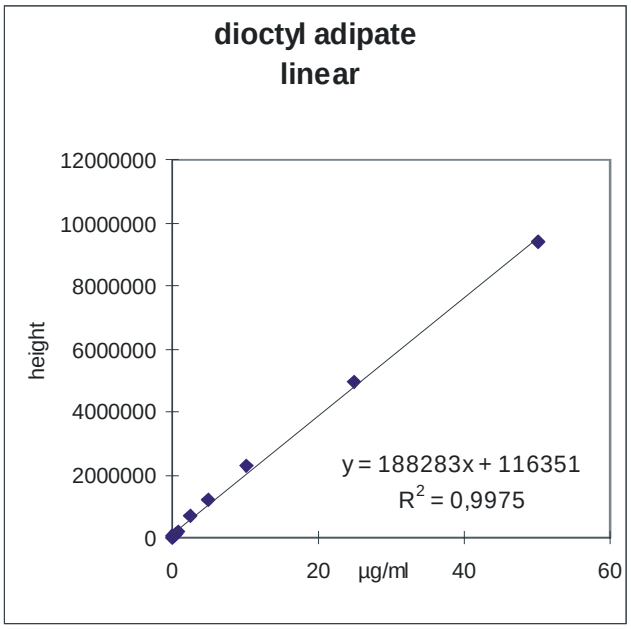

bis(2-ethylhexyl) adipate curve
height
µg/ml
y = -354,36x2 + 187615x + 41950
R2 = 0,9996

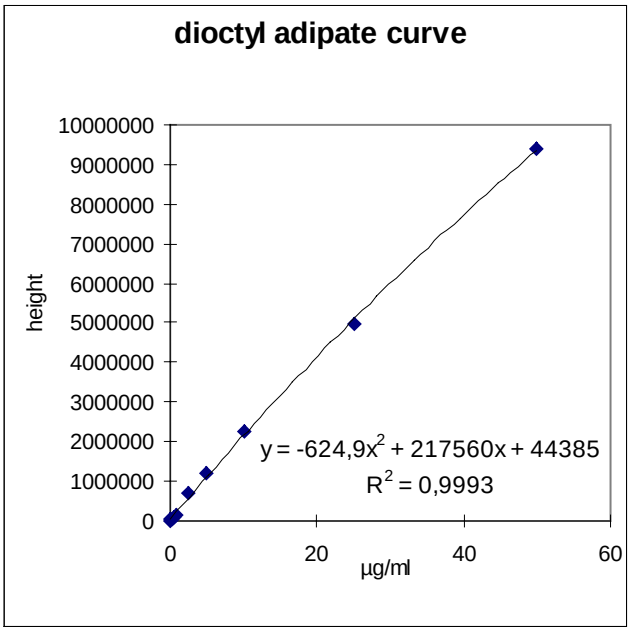

bis[2-(2-butoxyethoxy)ethyl]
adipate linear
height
µg/ml
y = 108301x + 21970
R2 = 0,9995

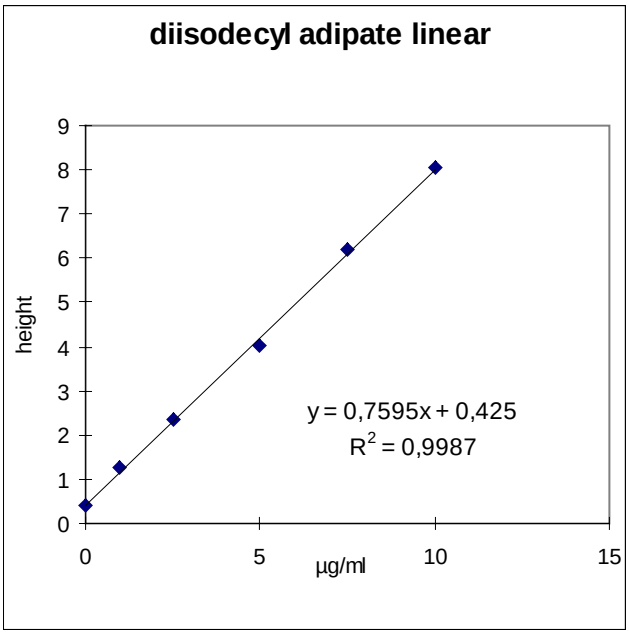

bis[2-(2-butoxyethoxy)ethyl]
adipate curve
height
µg/ml
y = 55,098x2 + 105640x + 31055
R2 = 0,9995

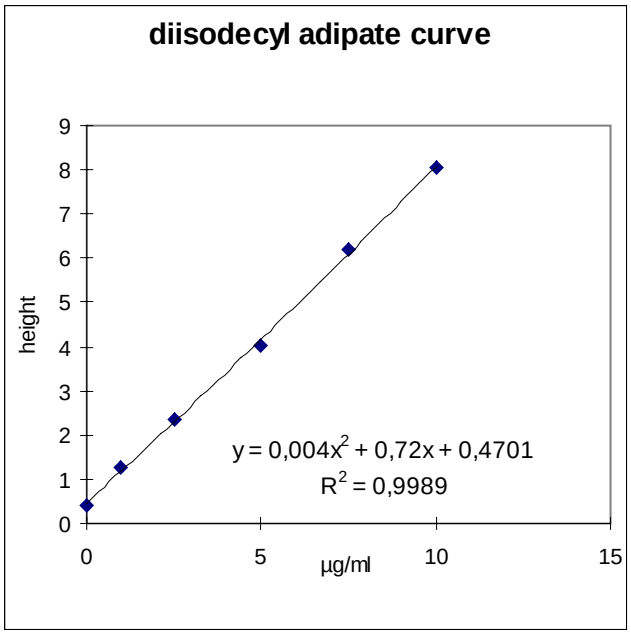

bis(2-butoxyethyl) adipate
linear
height
µg/ml
y = 136083x + 54642
R2 = 0,9992

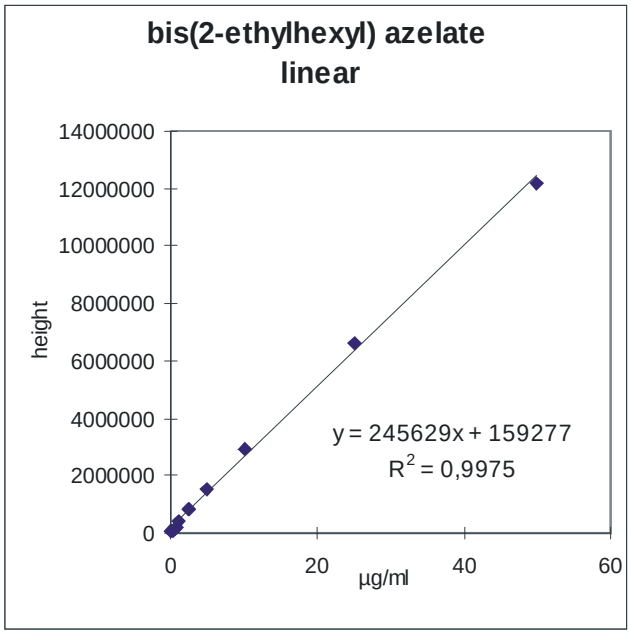

bis(2-butoxyethyl) adipate curve
height
µg/ml
y = -87,641x2 + 140208x + 43968
R2 = 0,9993

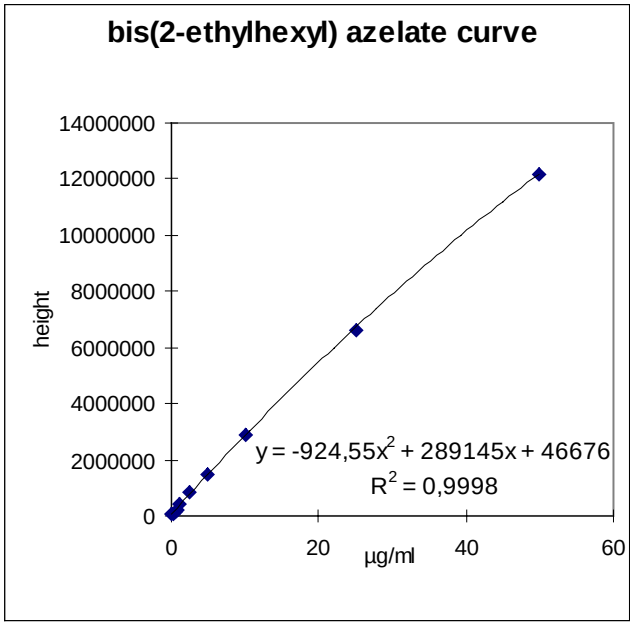

dioctyl adipate
linear
height
µg/ml
y = 188283x + 116351
R2 = 0,9975

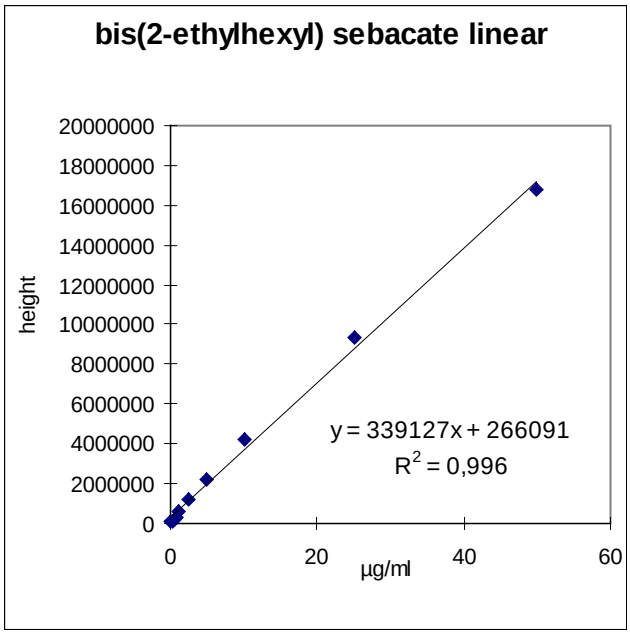

dioctyl adipate curve
height
µg/ml
y = -624,9x2 + 217560x + 44385
R2 = 0,9993

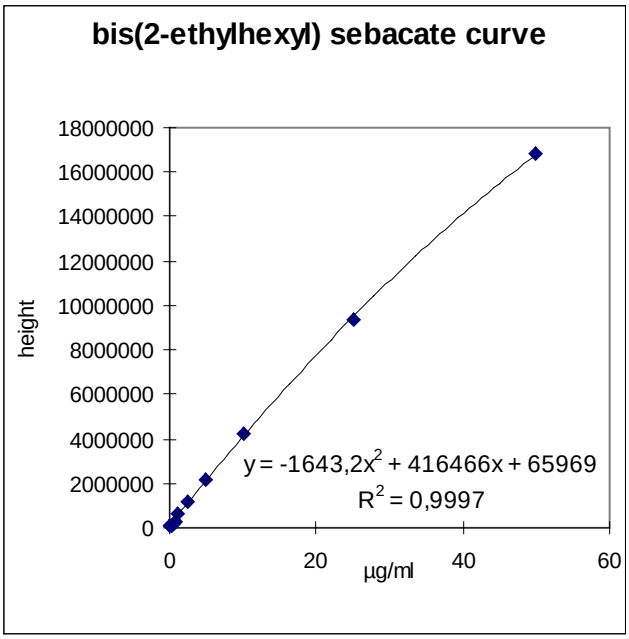

diisodecyl adipate linear
height
µg/ml
y = 0,7595x + 0,425
R2 = 0,9987

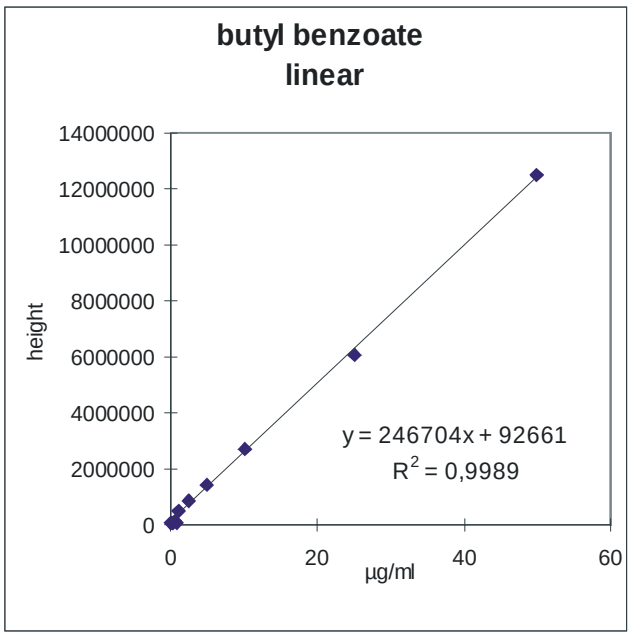

diisodecyl adipate curve
height
µg/ml
y = 0,004x2 + 0,72x + 0,4701
R2 = 0,9989

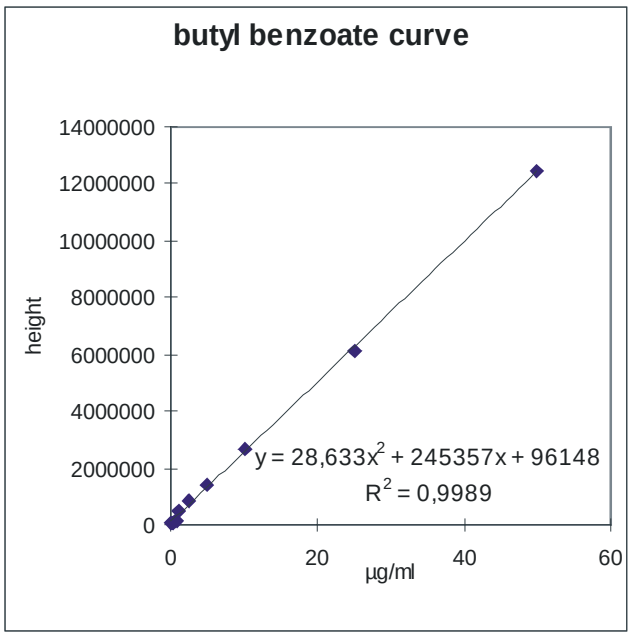

bis(2-ethylhexyl) azelate linear
height
µg/ml
y = 245629x + 159277
R2 = 0,9975

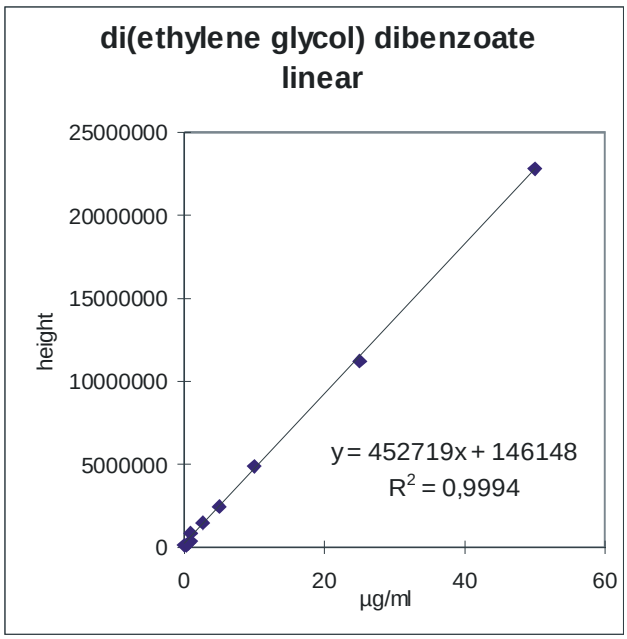

bis(2-ethylhexyl) azelate curve
height
µg/ml
y = -924,55x2 + 289145x + 46676
R2 = 0,9998

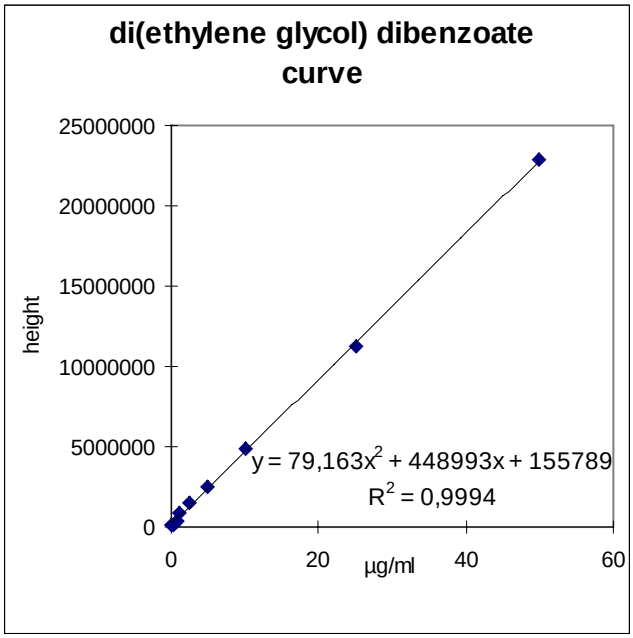

bis(2-ethylhexyl) sebacate linear
height
µg/ml
y = 339127x + 266091
R2 = 0,996

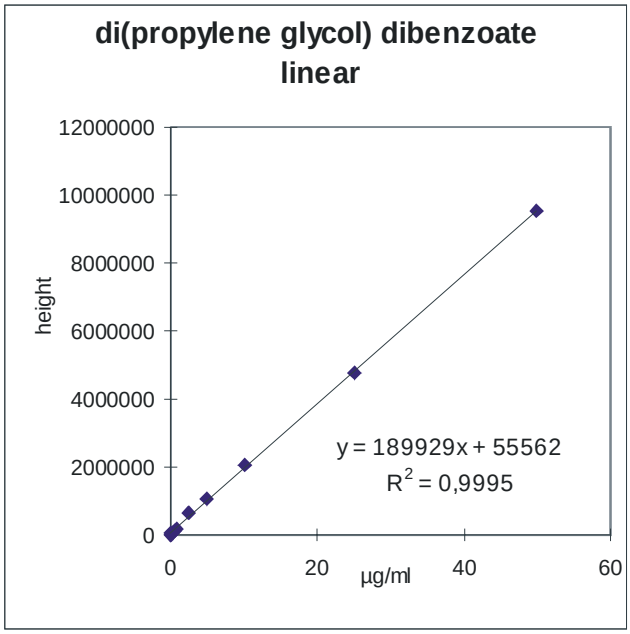

bis(2-ethylhexyl) sebacate curve
height
µg/ml
y = -1643,2x2 + 416466x + 65969
R2 = 0,9997

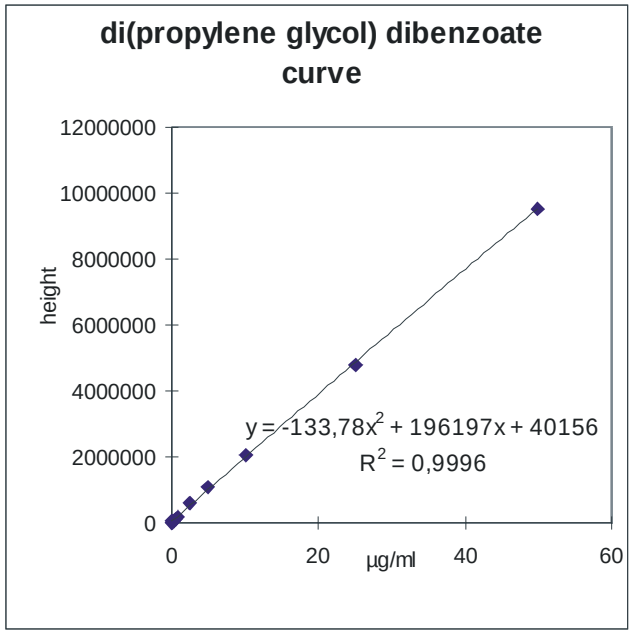

butyl benzoate linear
height
µg/ml
y = 246704x + 92661
R2 = 0,9989

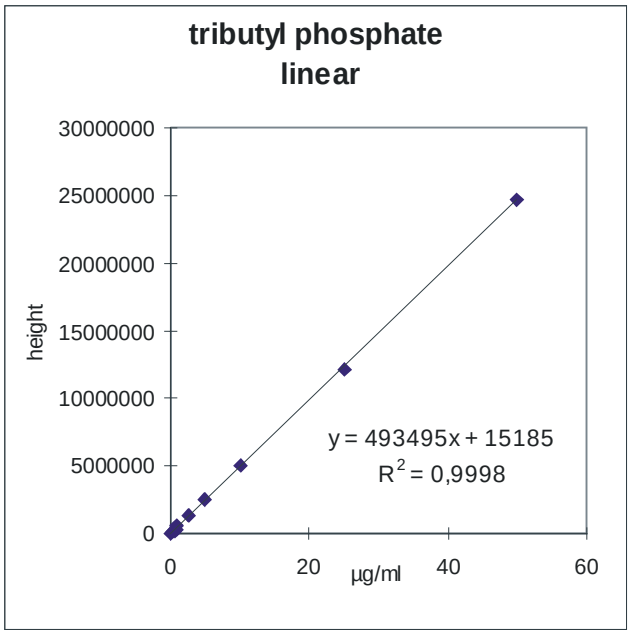

butyl benzoate curve
height
µg/ml
y = 28,633x2 + 245357x + 96148
R2 = 0,9989

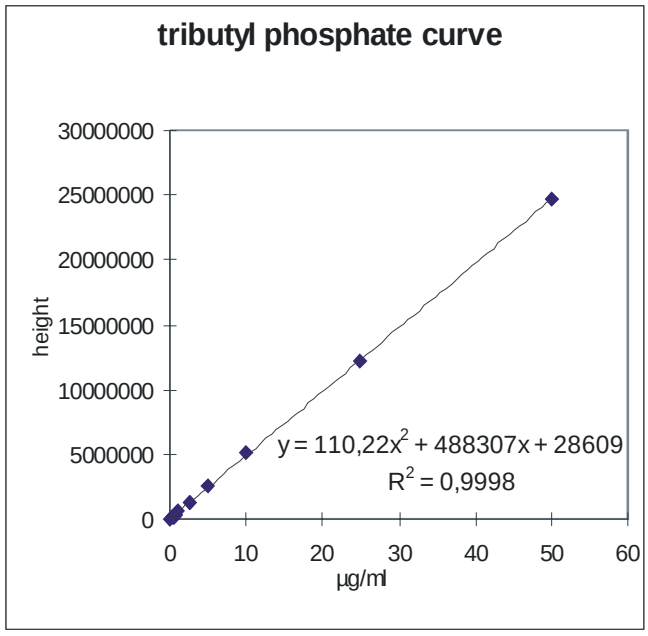

di(ethylene glycol) dibenzoate linear
height
µg/ml
y = 452719x + 146148
R2 = 0,9994

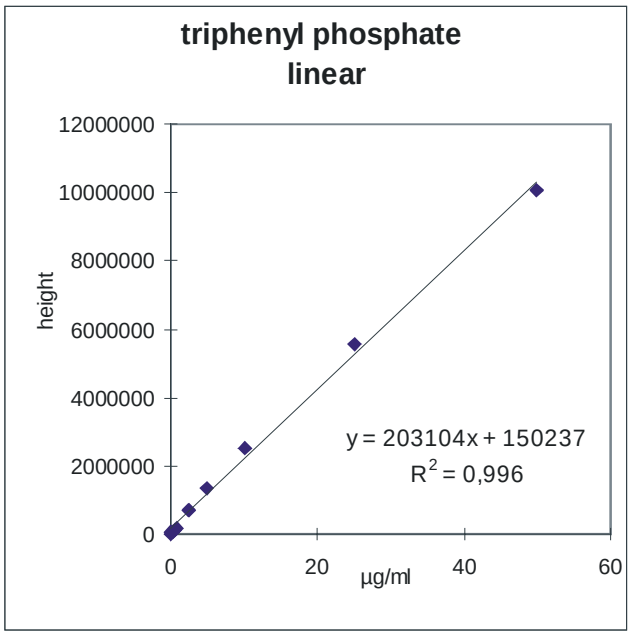

di(ethylene glycol) dibenzoate curve
height
µg/ml
y = 79,163x2 + 448993x + 155789
R2 = 0,9994

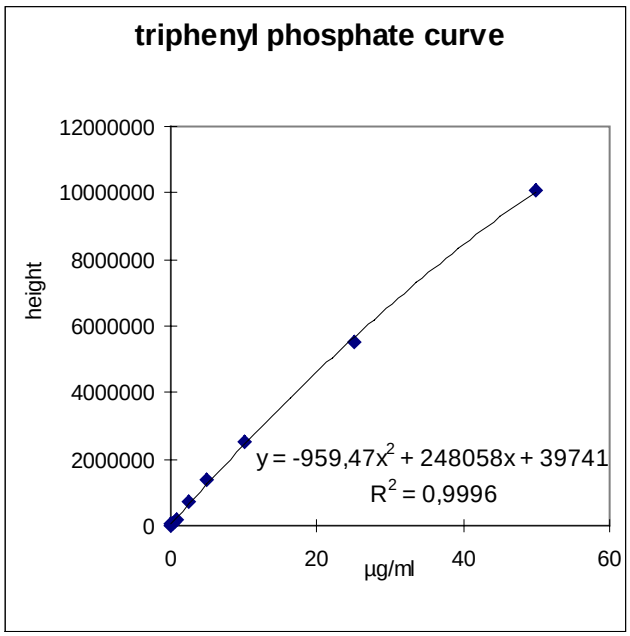

di(propylene glycol) dibenzoate linear
height
µg/ml
y = 189929x + 55562
R2 = 0,9995

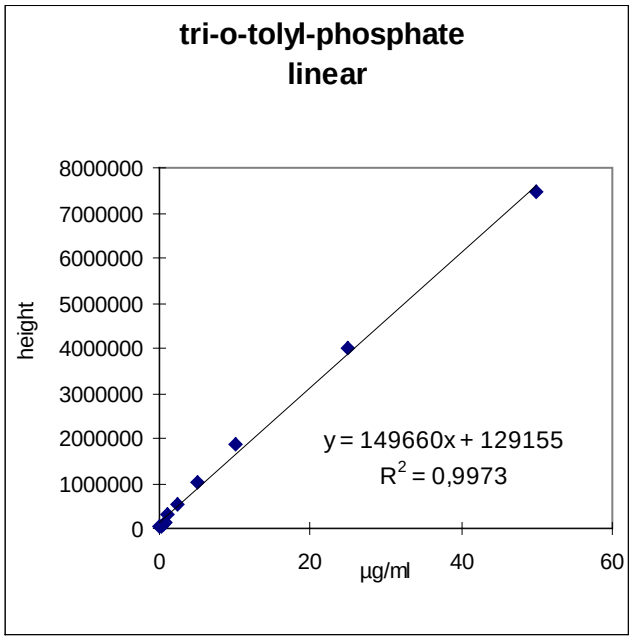

di(propylene glycol) dibenzoate curve
height
µg/ml
y = -133,78x2 + 196197x + 40156
R2 = 0,9996

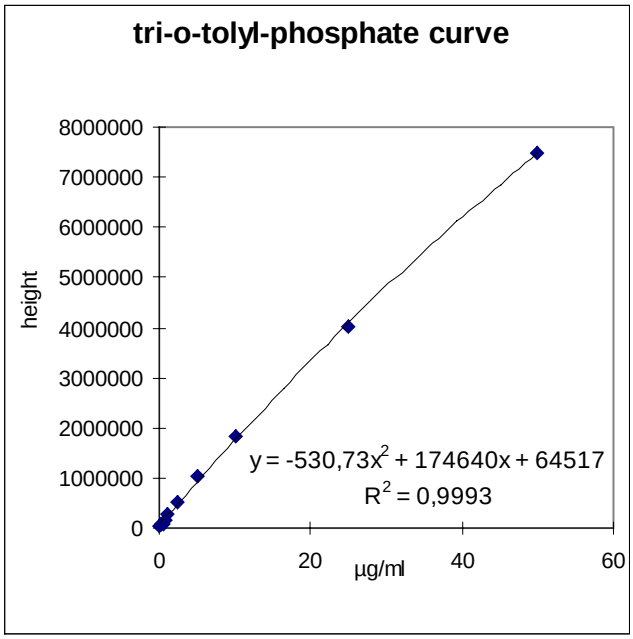

tributyl phosphate linear
height
µg/ml
y = 493495x + 15185
R2 = 0,9998

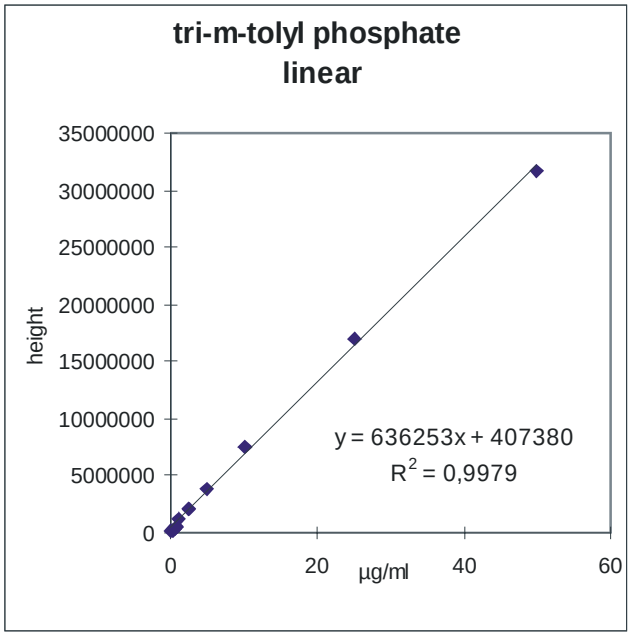

tributyl phosphate curve
height
µg/ml
y = 110,22x2 + 488307x + 28609
R2 = 0,9998

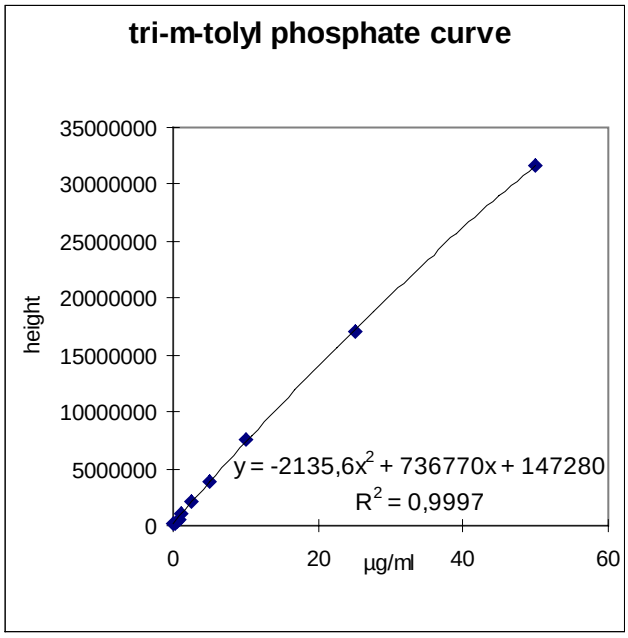

triphenyl phosphate linear
height
µg/ml
y = 203104x + 150237
R2 = 0,996

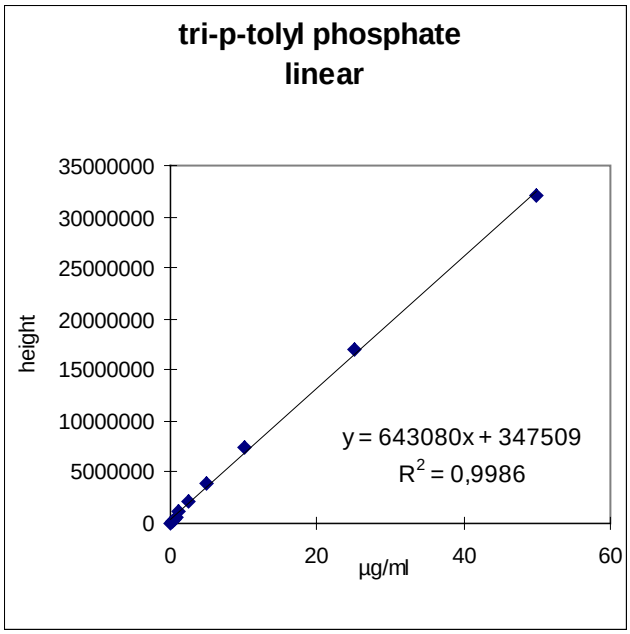

triphenyl phosphate curve
height
µg/ml
y = -959,47x2 + 248058x + 39741
R2 = 0,9996

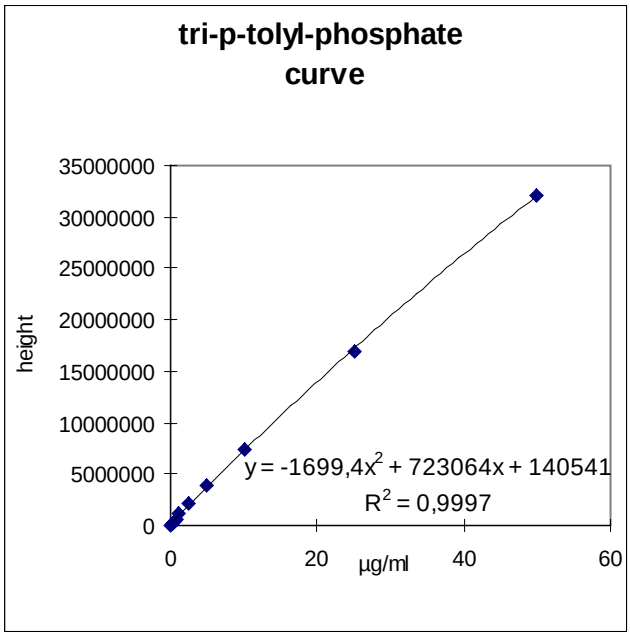

tri-o-tolyl-phosphate linear
height
µg/ml
y = 149660x + 129155
R2 = 0,9973

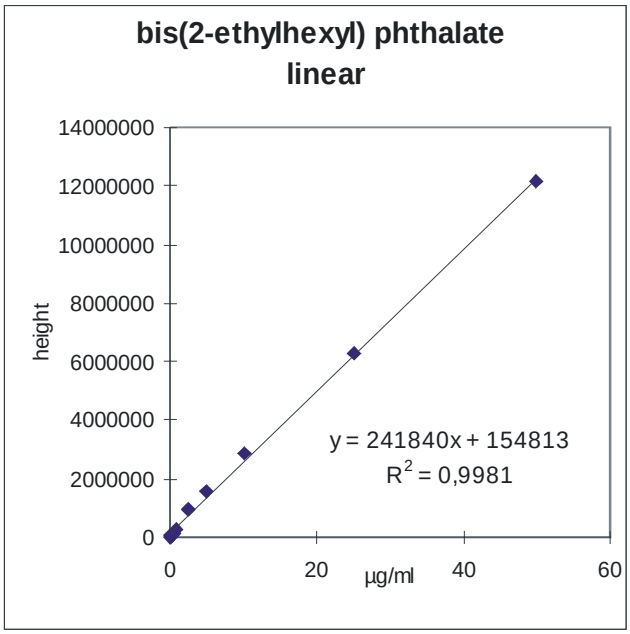

tri-o-tolyl-phosphate curve
height
µg/ml
y = -530,73x2 + 174640x + 64517
R2 = 0,9993

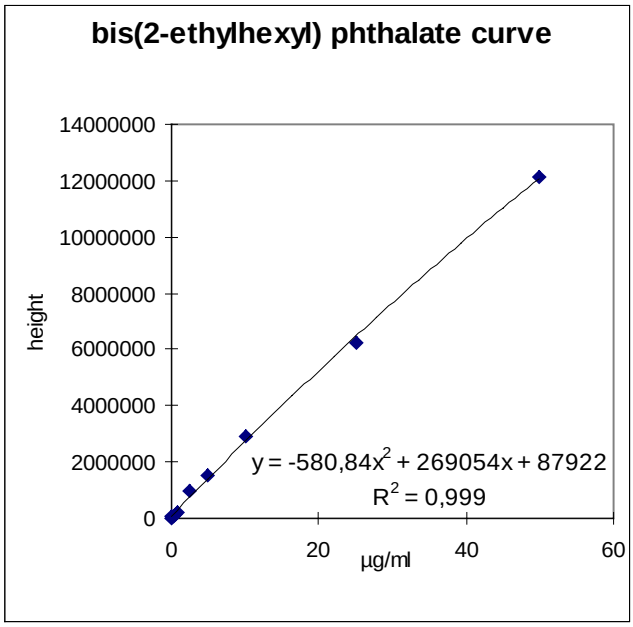

tri-m-tolyl phosphate linear
height
µg/ml
y = 636253x + 407380
R2 = 0,9979

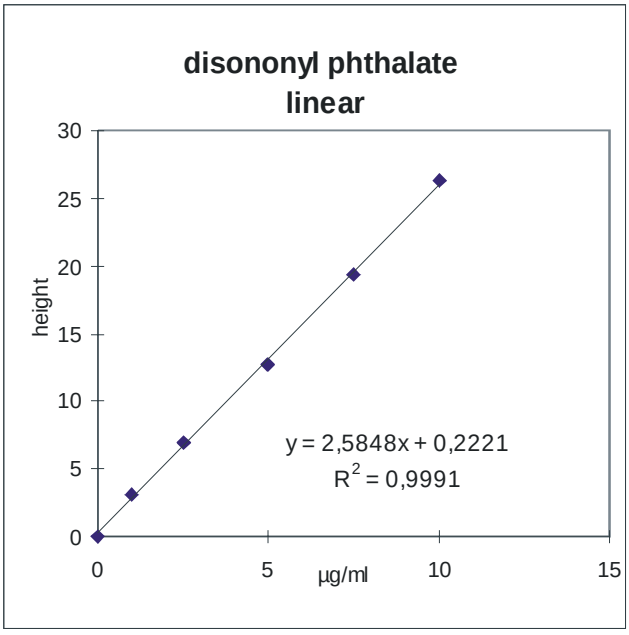

tri-m-tolyl phosphate curve
height
µg/ml
y = -2135,6x2 + 736770x + 147280
R2 = 0,9997

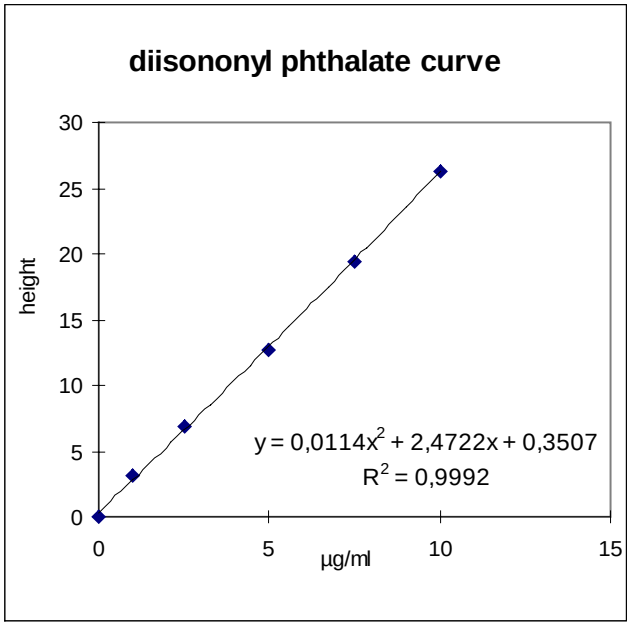

tri-p-tolyl phosphate
linear
height
µg/ml
y = 643080x + 347509
R2 = 0,9986


tri-p-tolyl-phosphate
curve
height
µg/ml
y = -1699,4x2 + 723064x + 140541
R2 = 0,9997


bis(2-ethylhexyl) phthalate
linear
height
µg/ml
y = 241840x + 154813
R2 = 0,9981


bis(2-ethylhexyl) phthalate curve
height
µg/ml
y = -580,84x2 + 269054x + 87922
R2 = 0,999


disononyl phthalate
linear
height
µg/ml
y = 2,5848x + 0,2221
R2 = 0,9991


diisononyl phthalate curve
height
µg/ml
y = 0,0114x2 + 2,4722x + 0,3507
R2 = 0,9992

3.2 Recovery

The recovery experiments of the plasticizers from water were performed on the 50%-level from the proposed limits. For some substances the detection limit had to be determined by the lead laboratory (ND = Not detectable). In those cases the recovery experiments were carried out at a concentration of 6µg/100ml water (=50% of the limit established for bis(2-ethylhexyl) phthalate). The ND level for the listed phosphates was estimated to be about 1µg/100ml H_20 (0,1µg/ml solvent).

Concentrations for recovery experiments:

Substance	**CAS Number**	**Limit in 100ml H_20**	**Conc. in 100ml H_2O**
Tributyl citrate	77-94-1	170µg	85µg
Tributyl *O*-acetyl citrate	77-90-7	170µg	85µg
Triethyl citrate	77-93-0	170µg	85µg
Triethyl *O*-acetyl citrate	77-89-4	170µg	85µg
Bis(2-ethylhexyl) adipate	103-23-1	100µg	50µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	170µg	85µg
Bis(2-butoxyethyl) adipate	141-18-4	170µg	85µg
Dioctyl adipate	123-79-5	170µg	85µg
Diisodecyl adipate	27178-16-1	170µg	85µg
Bis(2-ethylhexyl) azelate	103-24-2	170µg	85µg
Bis(2-ethylhexyl) sebacate	122-62-3	170µg	85µg
Butyl benzoate	136-60-7	1700µg as benzoic acid	850µg as benzoic acid
Di(ethylene glycol) dibenzoate	120-55-8	1700µg	850µg
Di(propylene glycol) dibenzoate	94-51-9	1700µg	850µg
Tributyl phosphate	126-73-8	170µg	85µg
Triphenyl phosphate	115-86-6	ND	6µg
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	ND	6µg
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	ND	6µg
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	ND	6µg
Bis (2-ethylhexyl) phthalate	117-81-7	12µg	6µg
Diisononyl phthalate	68515-48-0	50µg	25µg

A stock solution in acetone was prepared containing all substances at the following concentration levels:

Substance	**Concentration [mg/ml]**
Tributyl citrate	1,714
Tributyl O-acetyl citrate	1,723
Triethyl citrate	1,704
Triethyl O-acetyl citrate	1,702
Bis(2-ethylhexyl) adipate	1,710
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,700
Bis(2-butoxyethyl) adipate	1,702
Dioctyl adipate	1,700
Diisodecyl adipate	1,698
Bis(2-ethylhexyl) azelate	1,699
Bis(2-ethylhexyl) sebacate	1,755
Butyl benzoate (*)	24,793
Di(ethylene glycol) dibenzoate	17,007
Di(propylene glycol) dibenzoate	17,004
Tributyl phosphate	1,698
Triphenyl phosphate*	0,1213
Tri-*o*-cresyl phosphate	0,123
Tri-*m*-tolyl phosphate	0,1201
Tri-*p*-tolyl phosphate	0,1196
Bis (2-ethylhexyl) phthalate	0,1238
Diisononyl phthalate	0,4996

(*) The concentration of butyl benzoate was chosen to obtain a level of 17mg/ml as benzoic acid.

0,5ml of this solution was added to 1l of deionized water to obtain the concentrations shown in the previous table. In addition, 50µl of a solution of benzylbutyl phthalate in acetone (c=10mg/ml) was added as internal standard (corresponding to 50µg/100ml H_2O).

Homogenisation of this solution was not possible. Even after mechanical shaking for 30 minutes there were still small droplets of organic matter visible. So 1ml of pure acetone was added to ensure a homogenised sample.

100ml of the homogenised sample were extracted with 10ml of organic solvent by shaking the sample in a separatory funnel for 1 minute.

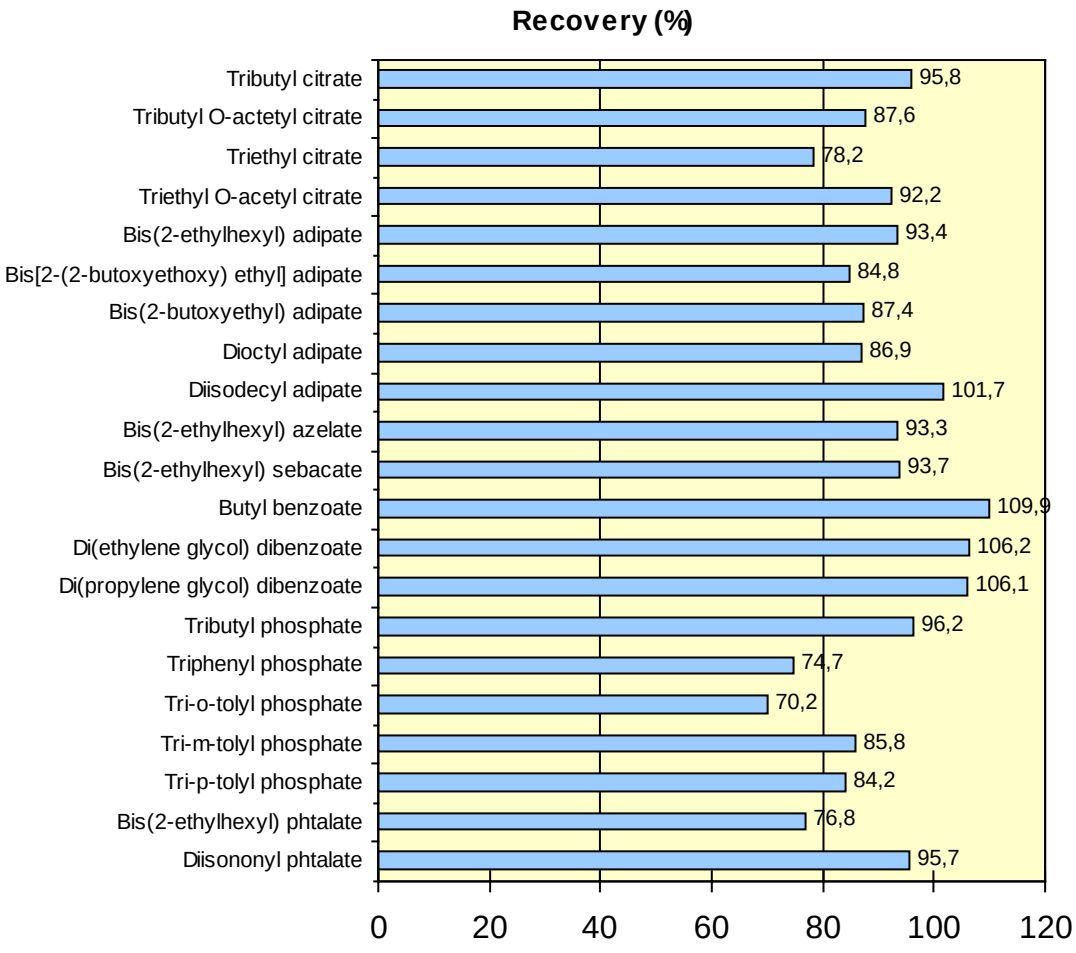
The following experiments were carried out:

Sample extracted with toluene, heptane, hexane, cyclohexane and toluene:ethylacetate=95:5.
Sample with 5g of sodiumchloride, extraction with toluene and toluene:ethylacetate=95:5.
Sample with 50g of sodiumchloride or 50g of magnesiumsulfate or 50g of disodiumhydrogenphosphate, extraction with toluene.
Sample with 5g of disodiumhydrogenphosphate or 0,5ml of phosphorous acid or 5ml of phosphorous acid and 5g of disodiumhydrogenphosphate, extraction with toluene.

Recovery experiments were carried out in duplicate. Results mentioned below are arithmetic means of both experiments. The values have been calculated taking into account the internal standard response.

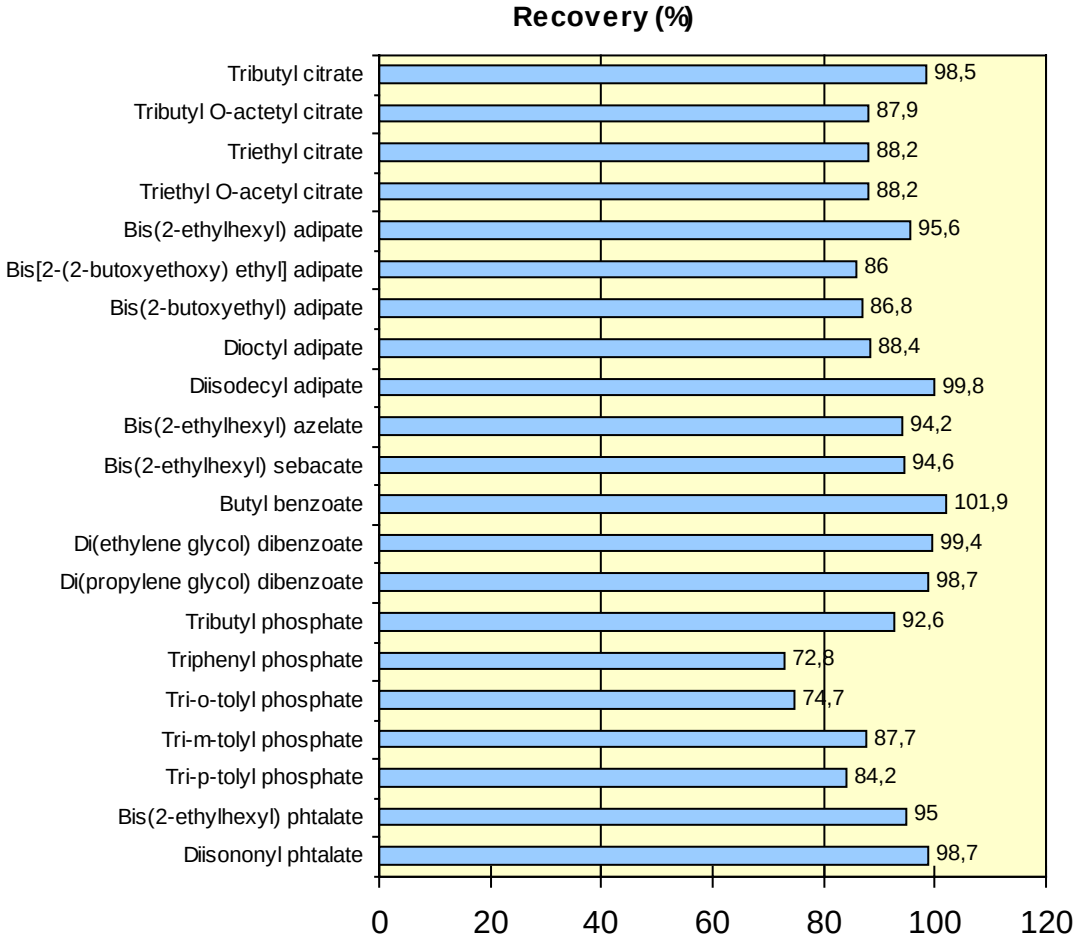
100ml water sample with 50g Na_2HPO_4, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	95,8
Tributyl O-acetyl citrate	87,6
Triethyl citrate	78,2
Triethyl O-acetyl citrate	92,2
Bis(2-ethylhexyl) adipate	93,4
Bis[2-(2-butoxyethoxy) ethyl] adipate	84,8
Bis(2-butoxyethyl) adipate	87,4
Dioctyl adipate	86,9
Diisodecyl adipate	101,7
Bis(2-ethylhexyl) azelate	93,3
Bis(2-ethylhexyl) sebacate	93,7
Butyl benzoate	109,9
Di(ethylene glycol) dibenzoate	106,2
Di(propylene glycol) dibenzoate	106,1
Tributyl phosphate	96,2
Triphenyl phosphate	74,7
Tri-*o*-tolyl phosphate	70,2
Tri-*m*-tolyl phosphate	85,8
Tri-*p*-tolyl phosphate	84,2
Bis(2-ethylhexyl) phthalate	76,8
Diisononyl phthalate	95,7



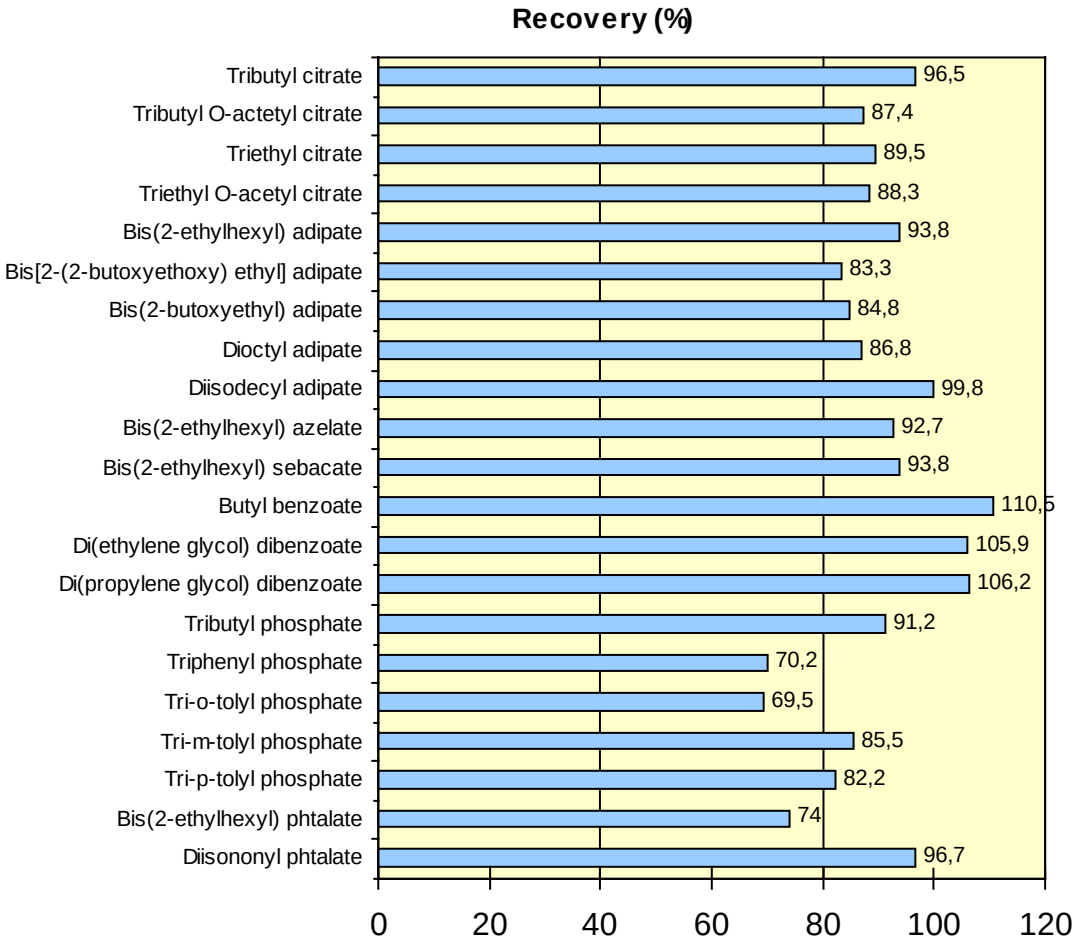
100ml water sample with 50g NaCl, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	98,5
Tributyl O-acetyl citrate	87,9
Triethyl citrate	88,2
Triethyl O-acetyl citrate	88,2
Bis(2-ethylhexyl) adipate	95,6
Bis[2-(2-butoxyethoxy) ethyl] adipate	86,0
Bis(2-butoxyethyl) adipate	86,8
Dioctyl adipate	88,4
Diisodecyl adipate	99,8
Bis(2-ethylhexyl) azelate	94,2
Bis(2-ethylhexyl) sebacate	94,6
Butyl benzoate	101,9
Di(ethylene glycol) dibenzoate	99,4
Di(propylene glycol) dibenzoate	98,7
Tributyl phosphate	92,6
Triphenyl phosphate	72,8
Tri-*o*-tolyl phosphate	74,7
Tri-*m*-tolyl phosphate	87,7
Tri-*p*-tolyl phosphate	83,7
Bis(2-ethylhexyl) phthalate	95,0
Diisononyl phthalate	98,7



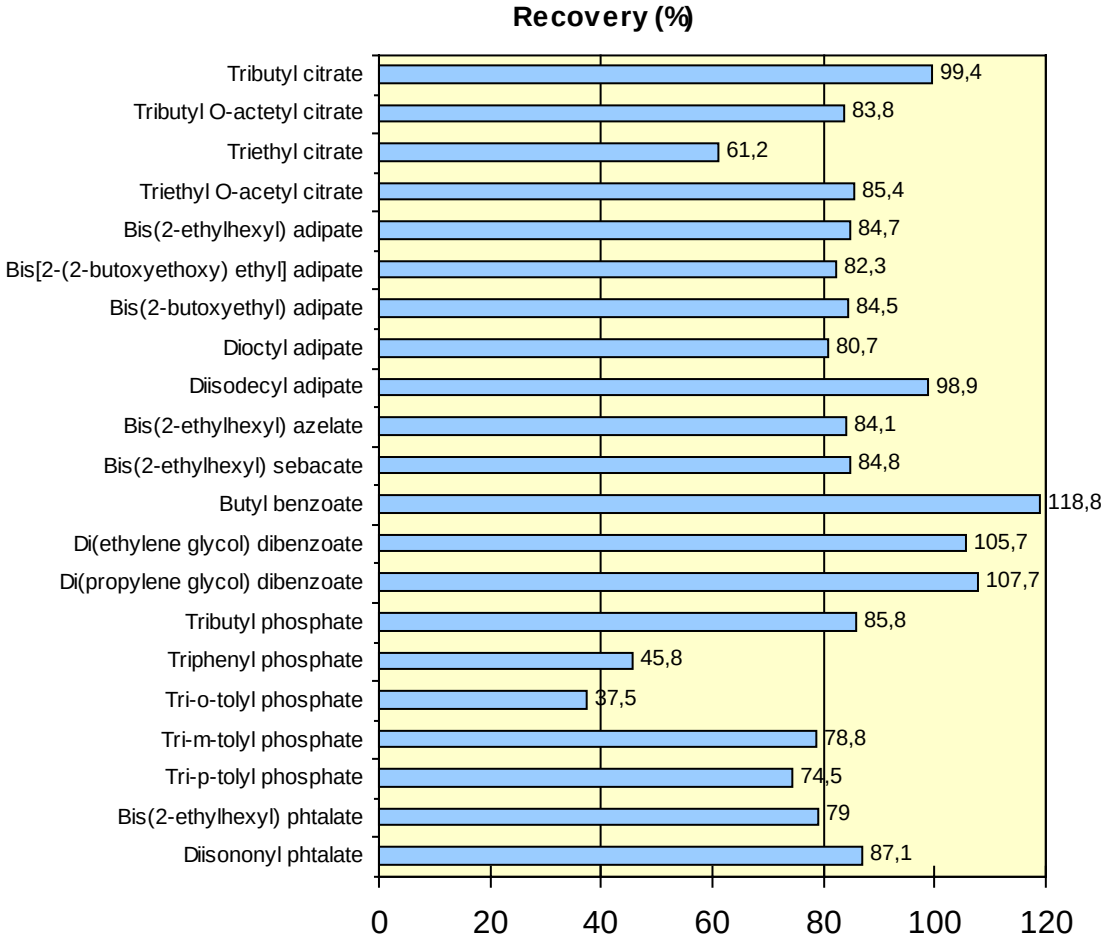
100ml water sample with 50g $MgSO_4$, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	96,5
Tributyl O-acetyl citrate	87,4
Triethyl citrate	89,5
Triethyl O-acetyl citrate	88,3
Bis(2-ethylhexyl) adipate	93,8
Bis[2-(2-butoxyethoxy) ethyl] adipate	83,3
Bis(2-butoxyethyl) adipate	84,8
Dioctyl adipate	86,8
Diisodecyl adipate	99,8
Bis(2-ethylhexyl) azelate	92,7
Bis(2-ethylhexyl) sebacate	93,8
Butyl benzoate	110,5
Di(ethylene glycol) dibenzoate	105,9
Di(propylene glycol) dibenzoate	106,2
Tributyl phosphate	91,2
Triphenyl phosphate	70,2
Tri-*o*-tolyl phosphate	69,5
Tri-*m*-tolyl phosphate	85,5
Tri-*p*-tolyl phosphate	82,2
Bis(2-ethylhexyl) phthalate	74,0
Diisononyl phthalate	96,7



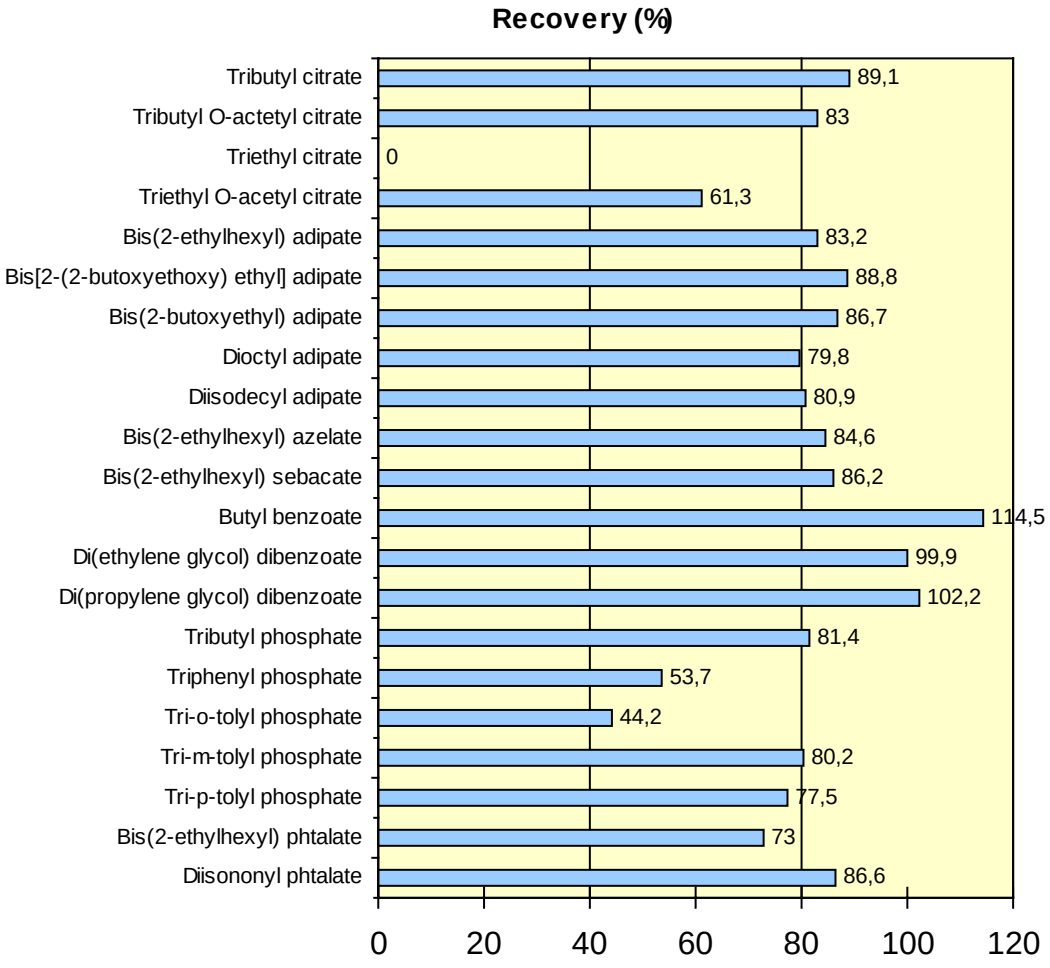
100ml water sample extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	99,4
Tributyl O-acetyl citrate	83,8
Triethyl citrate	61,2
Triethyl O-acetyl citrate	85,4
Bis(2-ethylhexyl) adipate	84,7
Bis[2-(2-butoxyethoxy) ethyl] adipate	82,3
Bis(2-butoxyethyl) adipate	84,5
Dioctyl adipate	80,7
Diisodecyl adipate	98,9
Bis(2-ethylhexyl) azelate	84,1
Bis(2-ethylhexyl) sebacate	84,8
Butyl benzoate	118,8
Di(ethylene glycol) dibenzoate	105,7
Di(propylene glycol) dibenzoate	107,7
Tributyl phosphate	85,8
Triphenyl phosphate	45,8
Tri-*o*-tolyl phosphate	37,5
Tri-*m*-tolyl phosphate	78,8
Tri-*p*-tolyl phosphate	74,5
Bis(2-ethylhexyl) phthalate	79,0
Diisononyl phthalate	87,1



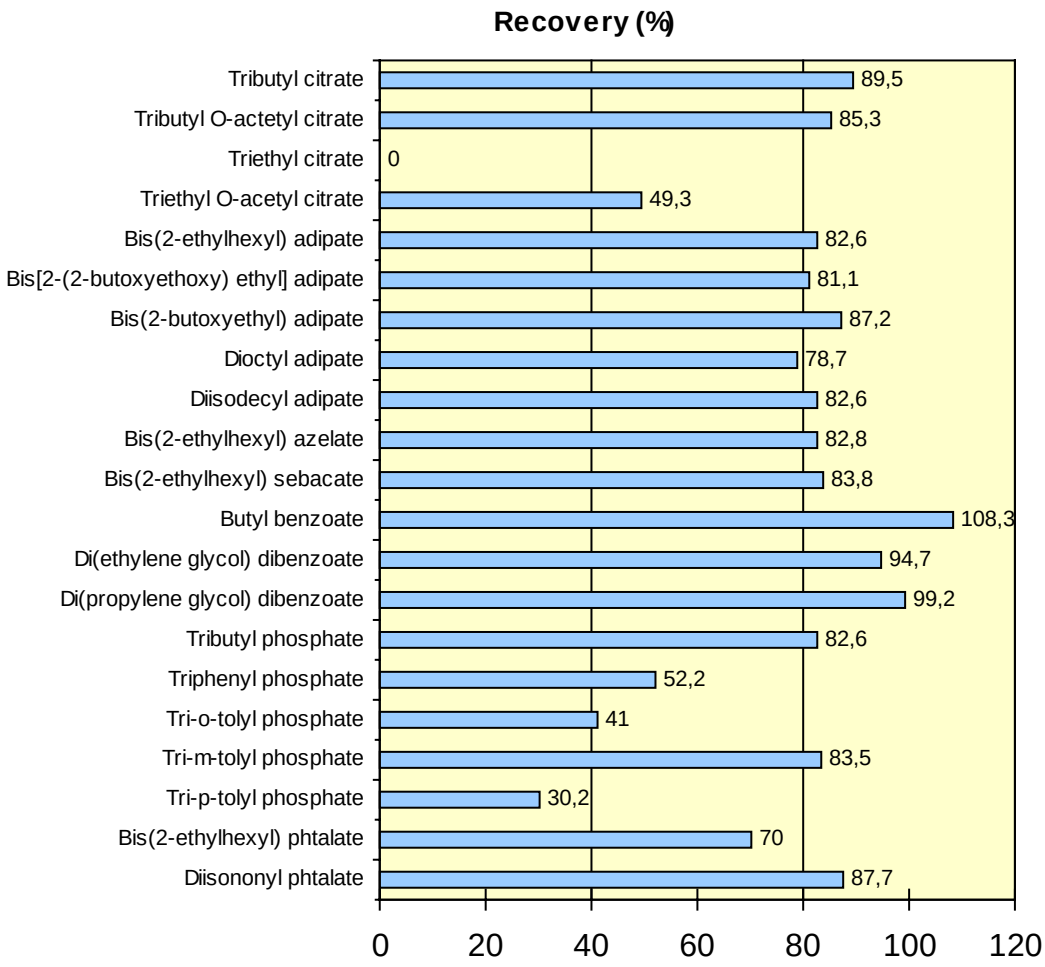
100ml water extracted with 10ml cyclohexane

Substance	Recovery [%]
Tributyl citrate	89,1
Tributyl O-acetyl citrate	83,0
Triethyl citrate	0,0
Triethyl O-acetyl citrate	61,3
Bis(2-ethylhexyl) adipate	83,2
Bis[2-(2-butoxyethoxy) ethyl] adipate	88,8
Bis(2-butoxyethyl) adipate	86,7
Dioctyl adipate	79,8
Diisodecyl adipate	80,9
Bis(2-ethylhexyl) azelate	84,6
Bis(2-ethylhexyl) sebacate	86,2
Butyl benzoate	114,5
Di(ethylene glycol) dibenzoate	99,9
Di(propylene glycol) dibenzoate	102,2
Tributyl phosphate	81,4
Triphenyl phosphate	53,7
Tri-*o*-tolyl phosphate	44,2
Tri-*m*-tolyl phosphate	80,2
Tri-*p*-tolyl phosphate	77,5
Bis(2-ethylhexyl) phtalate	73,0
Diisononyl phthalate	86,6



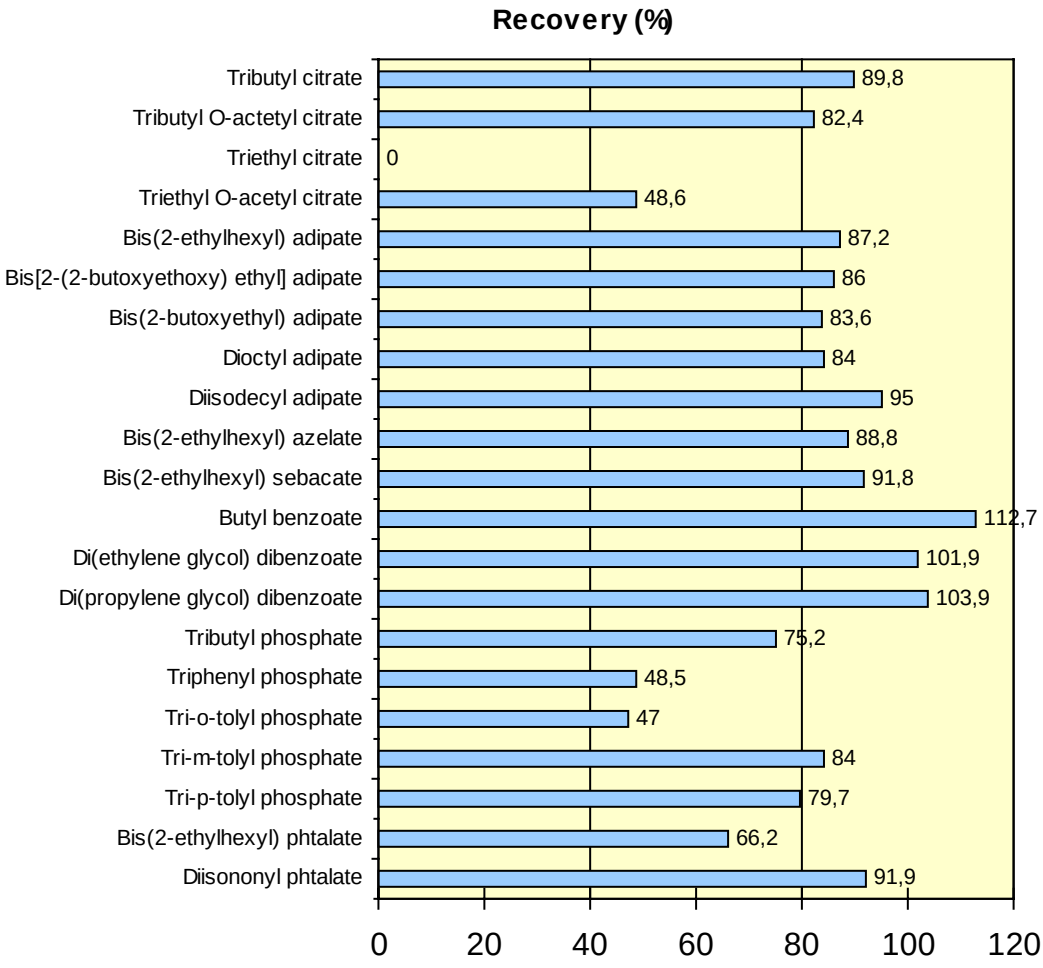
100ml water sample extracted with 10ml heptane

Substance	Recovery [%]
Tributyl citrate	89,5
Tributyl O-acetyl citrate	85,3
Triethyl citrate	0,0
Triethyl O-acetyl citrate	49,3
Bis(2-ethylhexyl) adipate	82,6
Bis[2-(2-butoxyethoxy) ethyl] adipate	81,1
Bis(2-butoxyethyl) adipate	87,2
Dioctyl adipate	78,7
Diisodecyl adipate	82,6
Bis(2-ethylhexyl) azelate	82,8
Bis(2-ethylhexyl) sebacate	83,8
Butyl benzoate	108,3
Di(ethylene glycol) dibenzoate	94,7
Di(propylene glycol) dibenzoate	99,2
Tributyl phosphate	82,6
Triphenyl phosphate	52,2
Tri-*o*-tolyl phosphate	41,0
Tri-*m*-tolyl phosphate	83,5
Tri-*p*-tolyl phosphate	30,2
Bis(2-ethylhexyl) phthalate	70,0
Diisononyl phthalate	87,7



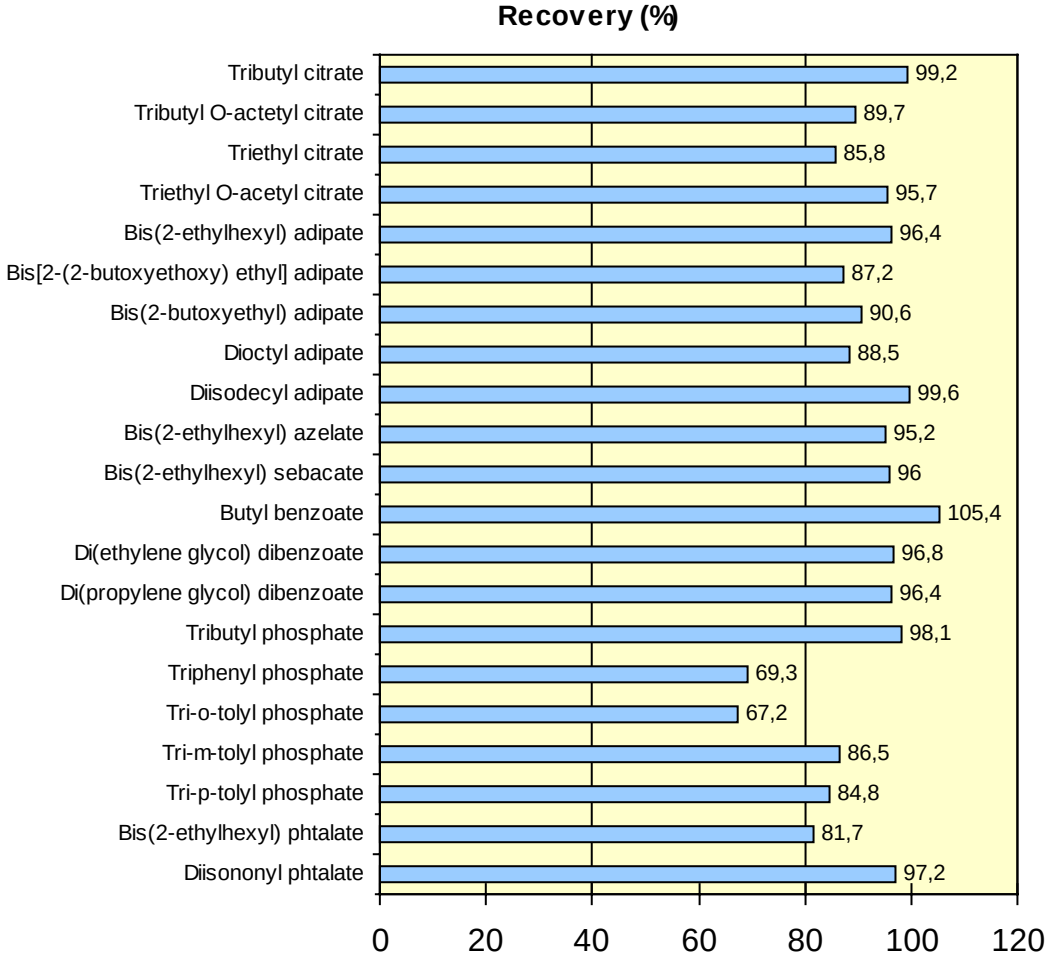
100ml water sample extracted with 10ml hexane

Substance	Recovery [%]
Tributyl citrate	89,8
Tributyl O-acetyl citrate	82,4
Triethyl citrate	0,0
Triethyl O-acetyl citrate	48,6
Bis(2-ethylhexyl) adipate	87,2
Bis[2-(2-butoxyethoxy) ethyl] adipate	86,0
Bis(2-butoxyethyl) adipate	83,6
Dioctyl adipate	84,0
Diisodecyl adipate	95,0
Bis(2-ethylhexyl) azelate	88,8
Bis(2-ethylhexyl) sebacate	91,8
Butyl benzoate	112,7
Di(ethylene glycol) dibenzoate	101,9
Di(propylene glycol) dibenzoate	103,9
Tributyl phosphate	75,2
Triphenyl phosphate	48,5
Tri-*o*-tolyl phosphate	47,0
Tri-*m*-tolyl phosphate	84,0
Tri-*p*-tolyl phosphate	79,7
Bis(2-ethylhexyl) phthalate	66,2
Diisononyl phthalate	91,9



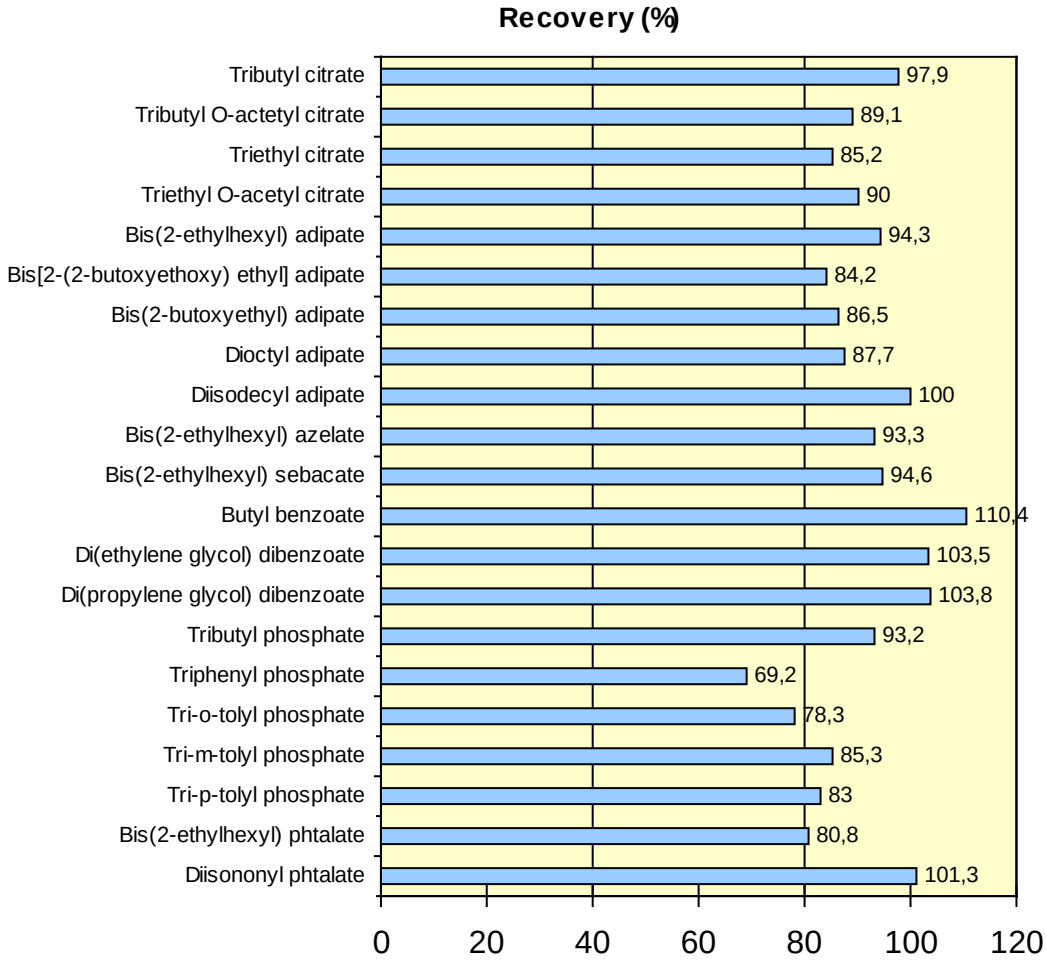
100ml water sample with 5g NaCl, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	99,2
Tributyl O-acetyl citrate	89,7
Triethyl citrate	85,8
Triethyl O-acetyl citrate	95,7
Bis(2-ethylhexyl) adipate	96,4
Bis[2-(2-butoxyethoxy) ethyl] adipate	87,2
Bis(2-butoxyethyl) adipate	90,6
Dioctyl adipate	88,5
Diisodecyl adipate	99,6
Bis(2-ethylhexyl) azelate	95,2
Bis(2-ethylhexyl) sebacate	96,0
Butyl benzoate	105,4
Di(ethylene glycol) dibenzoate	96,8
Di(propylene glycol) dibenzoate	96,4
Tributyl phosphate	98,1
Triphenyl phosphate	69,3
Tri-*o*-tolyl phosphate	67,2
Tri-*m*-tolyl phosphate	86,5
Tri-*p*-tolyl phosphate	84,8
Bis(2-ethylhexyl) phtalate	81,7
Diisononyl phthalate	97,2



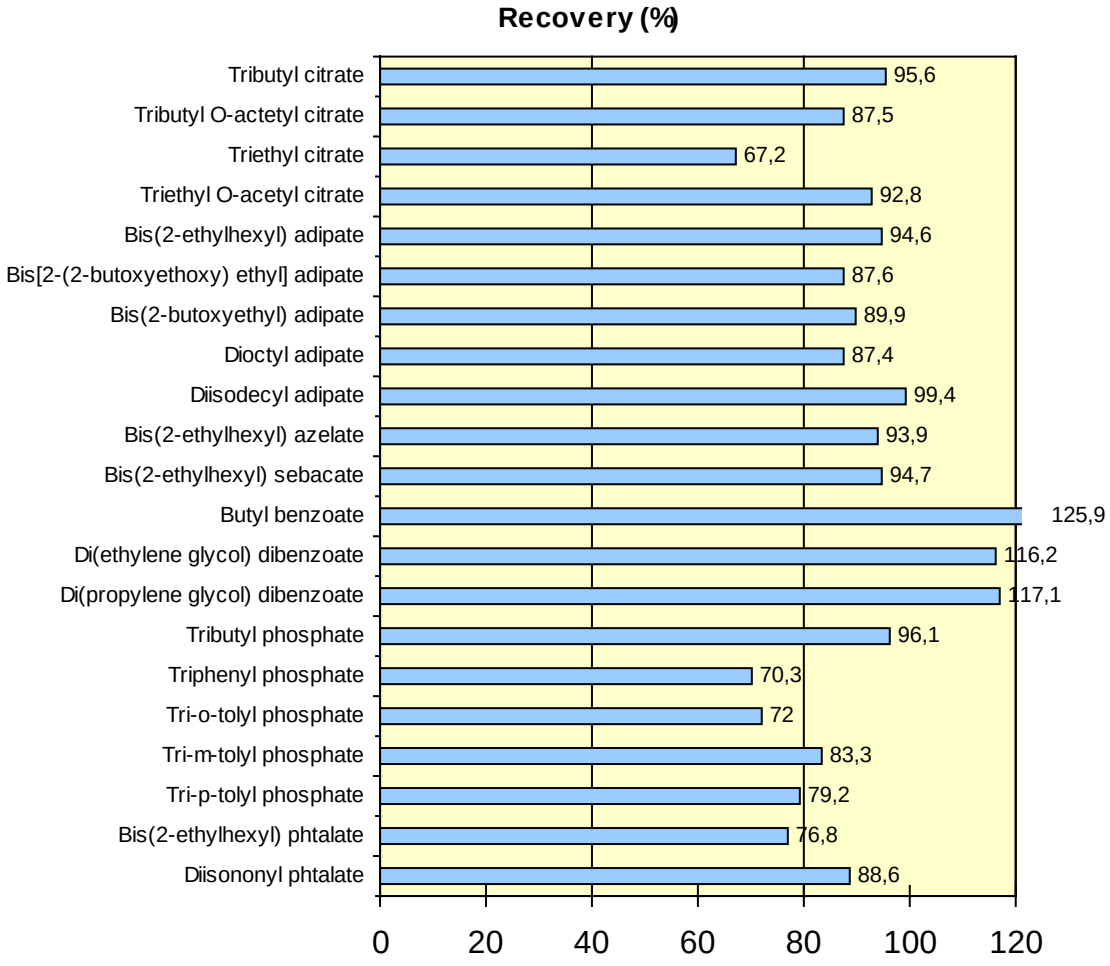
100ml water sample extracted with 10ml toluene:ethylacetate=95:5

Substance	Recovery [%]
Tributyl citrate	97,9
Tributyl O-acetyl citrate	89,1
Triethyl citrate	85,2
Triethyl O-acetyl citrate	90,0
Bis(2-ethylhexyl) adipate	94,3
Bis[2-(2-butoxyethoxy) ethyl] adipate	84,2
Bis(2-butoxyethyl) adipate	86,5
Dioctyl adipate	87,7
Diisodecyl adipate	100,0
Bis(2-ethylhexyl) azelate	93,3
Bis(2-ethylhexyl) sebacate	94,6
Butyl benzoate	110,4
Di(ethylene glycol) dibenzoate	103,5
Di(propylene glycol) dibenzoate	103,8
Tributyl phosphate	93,2
Triphenyl phosphate	69,2
Tri-*o*-tolyl phosphate	78,3
Tri-*m*-tolyl phosphate	85,3
Tri-*p*-tolyl phosphate	83,0
Bis(2-ethylhexyl) phthalate	80,8
Diisononyl phthalate	101,3



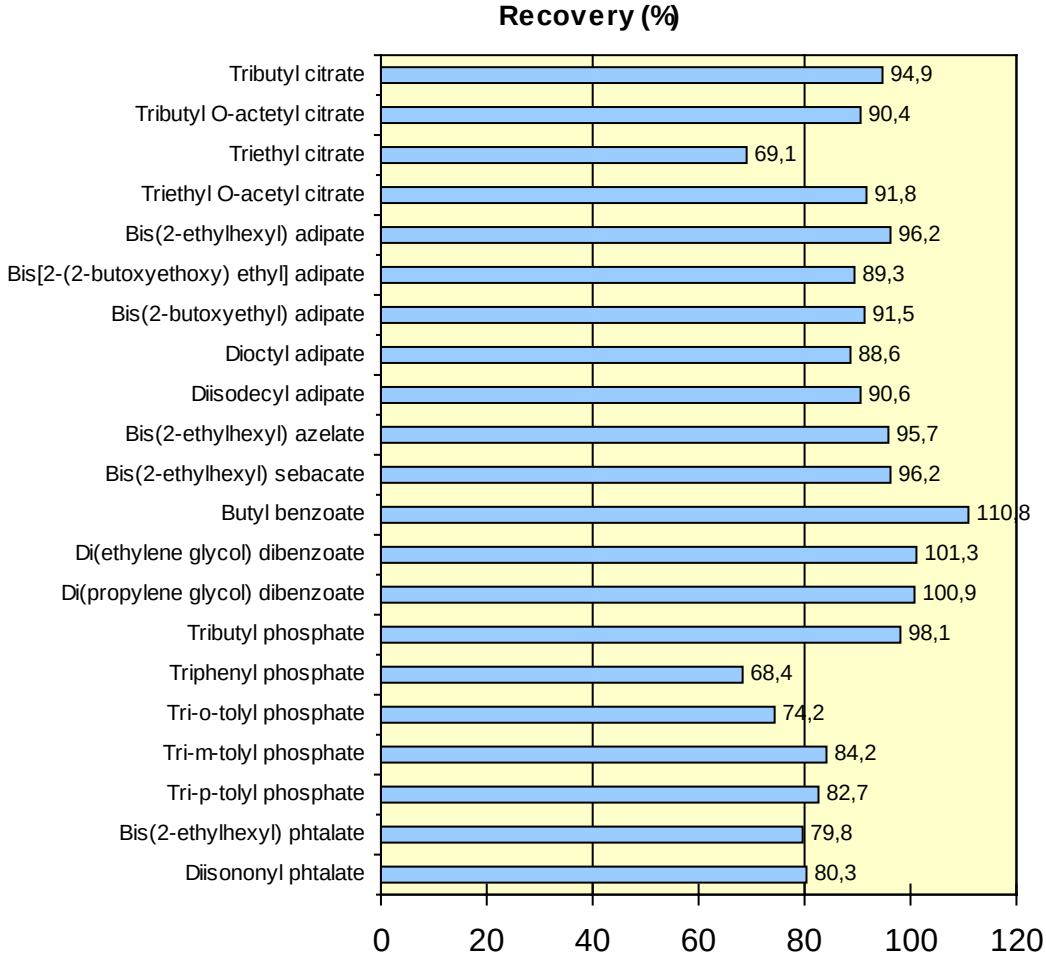
100ml water sample with 5g NaCl, extracted with 10ml toluene:ethylacetate=95:5

Substance	Recovery [%]
Tributyl citrate	95,6
Tributyl O-acetyl citrate	87,5
Triethyl citrate	67,2
Triethyl O-acetyl citrate	92,8
Bis(2-ethylhexyl) adipate	94,6
Bis[2-(2-butoxyethoxy) ethyl] adipate	87,6
Bis(2-butoxyethyl) adipate	89,9
Dioctyl adipate	87,4
Diisodecyl adipate	99,4
Bis(2-ethylhexyl) azelate	93,9
Bis(2-ethylhexyl) sebacate	94,7
Butyl benzoate	125,9
Di(ethylene glycol) dibenzoate	116,2
Di(propylene glycol) dibenzoate	117,1
Tributyl phosphate	96,1
Triphenyl phosphate	70,3
Tri-*o*-tolyl phosphate	72,0
Tri-*m*-tolyl phosphate	83,3
Tri-*p*-tolyl phosphate	79,2
Bis(2-ethylhexyl) phthalate	76,8
Diisononyl phthalate	88,6



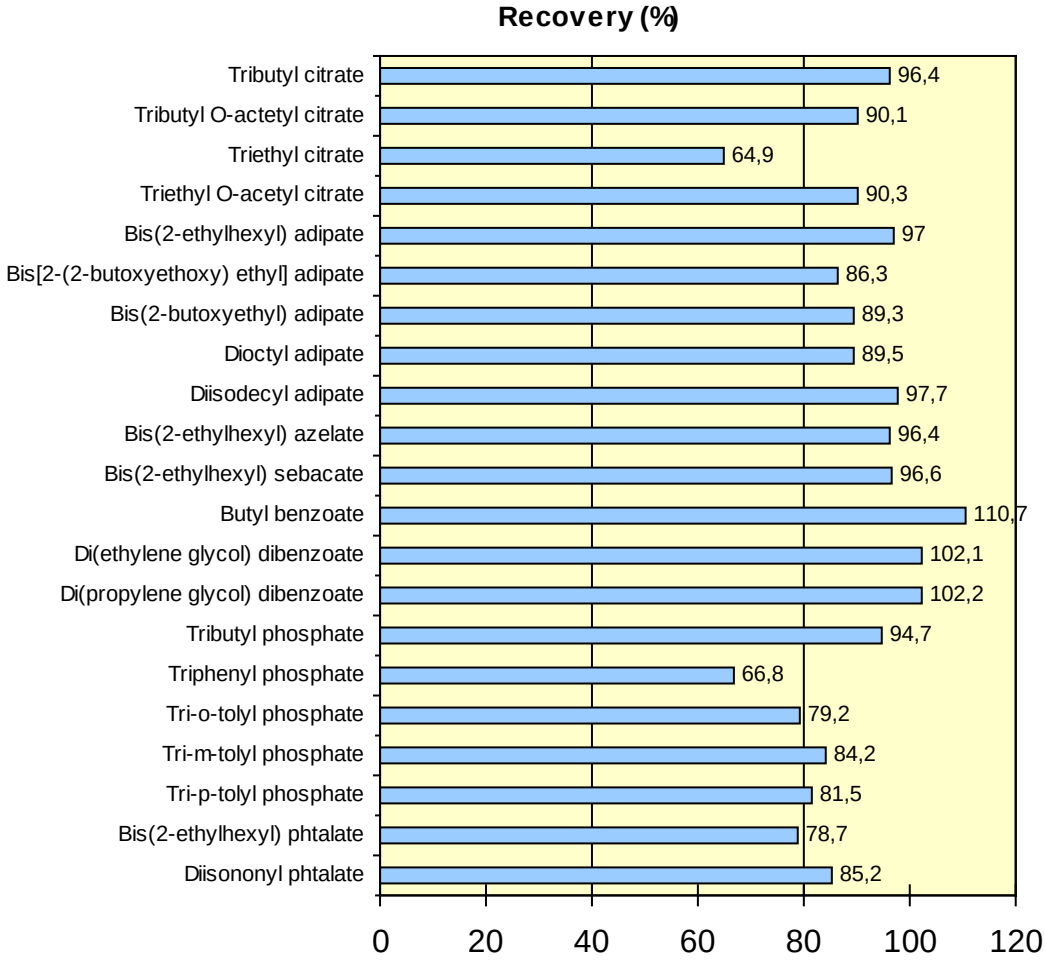
100ml water sample with 5g Na_2HPO4, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	94,9
Tributyl O-acetyl citrate	90,4
Triethyl citrate	69,1
Triethyl O-acetyl citrate	91,8
Bis(2-ethylhexyl) adipate	96,2
Bis[2-(2-butoxyethoxy) ethyl] adipate	89,3
Bis(2-butoxyethyl) adipate	91,5
Dioctyl adipate	88,6
Diisodecyl adipate	90,6
Bis(2-ethylhexyl) azelate	95,7
Bis(2-ethylhexyl) sebacate	96,2
Butyl benzoate	110,8
Di(ethylene glycol) dibenzoate	101,3
Di(propylene glycol) dibenzoate	100,9
Tributyl phosphate	98,1
Triphenyl phosphate	68,4
Tri-*o*-tolyl phosphate	74,2
Tri-*m*-tolyl phosphate	84,2
Tri-*p*-tolyl phosphate	82,7
Bis(2-ethylhexyl) phtalate	79,8
Diisononyl phthalate	80,3



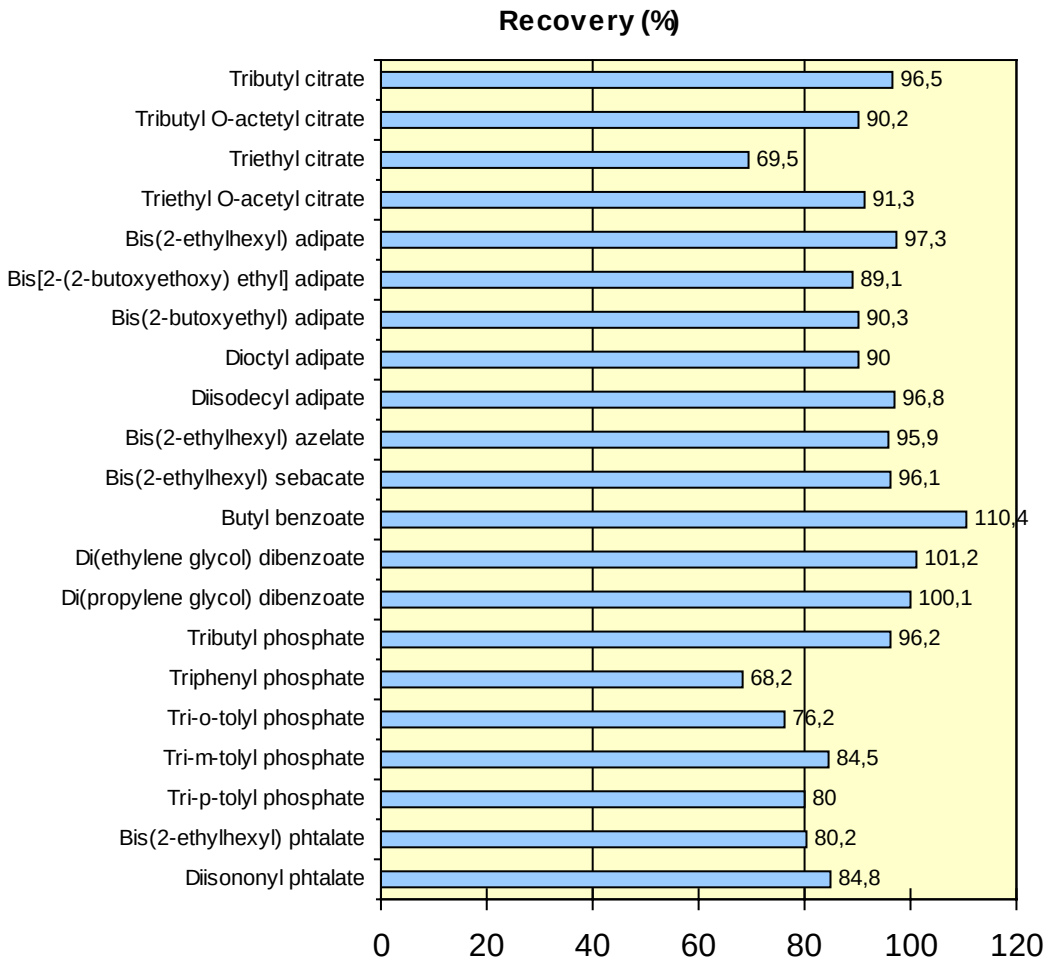
100ml water sample with 0,5ml H_3PO_4, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	96,4
Tributyl O-acetyl citrate	90,1
Triethyl citrate	64,9
Triethyl O-acetyl citrate	90,3
Bis(2-ethylhexyl) adipate	97,0
Bis[2-(2-butoxyethoxy) ethyl] adipate	86,3
Bis(2-butoxyethyl) adipate	89,3
Dioctyl adipate	89,5
Diisodecyl adipate	97,7
Bis(2-ethylhexyl) azelate	96,4
Bis(2-ethylhexyl) sebacate	96,6
Butyl benzoate	110,7
Di(ethylene glycol) dibenzoate	102,1
Di(propylene glycol) dibenzoate	102,2
Tributyl phosphate	94,7
Triphenyl phosphate	66,8
Tri-*o*-tolyl phosphate	79,2
Tri-*m*-tolyl phosphate	84,2
Tri-*p*-tolyl phosphate	81,5
Bis(2-ethylhexyl) phthalate	78,7
Diisononyl phthalate	85,2



100ml water sample with 0,5ml H_3PO_4 and 5g Na_2HPO4, extracted with 10ml toluene

Substance	Recovery [%]
Tributyl citrate	96,5
Tributyl O-acetyl citrate	90,2
Triethyl citrate	69,5
Triethyl O-acetyl citrate	91,3
Bis(2-ethylhexyl) adipate	97,3
Bis[2-(2-butoxyethoxy) ethyl] adipate	89,1
Bis(2-butoxyethyl) adipate	90,3
Dioctyl adipate	90,0
Diisodecyl adipate	96,8
Bis(2-ethylhexyl) azelate	95,9
Bis(2-ethylhexyl) sebacate	96,1
Butyl benzoate	110,4
Di(ethylene glycol) dibenzoate	101,2
Di(propylene glycol) dibenzoate	100,1
Tributyl phosphate	96,2
Triphenyl phosphate	68,2
Tri-*o*-tolyl phosphate	76,2
Tri-*m*-tolyl phosphate	84,5
Tri-*p*-tolyl phosphate	80,0
Bis(2-ethylhexyl) phthalate	80,2
Diisononyl phthalate	84,8



4 Discussion of Results

An analytical method was developed to analyse a wide variety of plasticizers in water using GC/MS. Usable analytical column, gaschromatograph- and mass spectrometer parameters are mentioned, in this report.

Numerous experiments have been carried out to determine extraction efficiency involving various solvents with and without addition of salts and phophoric acid.

The use of pure hexane, heptane, cyclohexane or toluene resulted in very poor recoveries for several plasticizers. Triethyl citrate was completely lost when hexane, heptane or cyclohexane was employed. The addition of salt or phosphoric acid led to increased recovery values.

Best results were achieved by using toluene:ethylacetate 95:5 and toluene with addition of 50g NaCl. In both cases the recoveries were normally above 80%. Only for 2 substances – triphenyl phosphate and tri-*o*-tolyl phosphate – recoveries were below 80% (with values between 70% and 80%). It was decided to select toluene:ethylacetate 95:5 for the further work.

Unfortunately the use of cyclohexane and heptane whose working place limits are roughly a factor of 5 above the limit of toluene and which would have been preferable from a health perspective cannot be used for performance reasons.

5 Validation

5.1 Introduction

This report describes the validation of the method for the determination of plasticizers circulated to CEN TC 52 WG9 TG2 as document N151.

In the method development we observed problems with the preparation of spiked water samples for recovery experiments. As a result of the limited solubility of several compounds it was necessary to add 1ml of acetone to get a homogenised sample. The initial recovery experiments were done at the 50% concentration only. However, the validation is required in a concentration range of 25% - 200%. From this follows that the amount of added plasticizers would have had to be increased by a factor up to 4.

It could be expected that this would have created even more difficulties with respect to solubility. The addition of more acetone could have resulted in a worsening of recovery values and was therefore judged not to be a good option. To compensate anticipated lower recovery values with repeated extraction would have made the method more time consuming and more expensive and would not have been desirable from an environmental point of view.

It was therefore decided to reduce the concentration of butyl benzoate, di(ethylene glycol)dibenzoate and di(propylene glycol) dibenzoate (these three substances make up more than 70% of the total organic load) by a factor of 10. Given that no limit has been established for the three plasticizers and that they have been included on voluntary basis in this study the choice seems to be justified.

Hence, the following substances and concentrations were used:

Substance	**CAS Number**	**in 100ml H_2O**
Tributyl citrate	77-94-1	170µg
Tributyl *O*-acetyl citrate	77-90-7	170µg
Triethyl citrate	77-93-0	170µg
Triethyl *O*-acetylcitrate	77-89-4	170µg
Bis(2-ethylhexyl) adipate	103-23-1	100µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	170µg
Bis(2-butoxyethyl) adipate	141-18-4	170µg
Dioctyl adipate	123-79-5	170µg
Diisodecyl adipate	27178-16-1	170µg
Bis(2-ethylhexyl) azelate	103-24-2	170µg
Bis(2-ethylhexyl) sebacate	122-62-3	170µg
Butyl benzoate	136-60-7	170µg as benzoic acid

Di(ethylene glycol) dibenzoate	120-55-8	170µg
Di(propylene glycol) dibenzoate	94-51-9	170µg
Tributyl phosphate	126-73-8	170µg
Triphenyl phosphate	115-86-6	ND (~1µg)*
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	ND (~1µg)*
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	ND (~1µg)*
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	ND (~1µg)*
Bis(2-ethylhexyl) phthalate	117-81-7	12µg
Diisononyl phthalate	68515-48-0	50µg

* ND=Not detectable, to be determined by lead laboratory, estimated to be about 1µg

Another difficulty was to follow the validation protocol for non detectable criteria (N142rev1). The document requires to determine the validation parameters on 3 concentration levels. However, it is neither adequate nor practical to determine linearity on the basis of 3 data points only because it is not clear from the beginning that an "ideal" straight line will be obtained. For non-linear regression curves at least 5 data points are needed. It is safer and less time consuming if sufficient data points are available (in case of non-compliance with the criteria the whole validation procedure would have to be repeated).

In addition, the concentration steps given in this document differ from the ones indicated in the protocol for method validation (N68rev4). The former uses 1x, 3x and 5x the limit of quantitation, the latter uses 25%, 50%, 100%, 150% and 200% of the limit which is 1x, 2x, 4x, 6x and 8x the 25% level.

In order to be able to determine linearity in accordance with N68rev4 and to be able to use the same dilution pattern for ND substances and substances with an estimated limit value the procedure for the validation of ND levels was slightly modified. In case of substances for which the ND value had to be determined (triphenyl phosphate and tricresyl phosphate isomers) the LOQ was estimated from the calibration data (signal/noise 9:1). The validation was done using 1x, 2x, 4x, 6x and 8x this level. Given that the validation was done with spiked water samples excluding toy materials it was felt that a safety margin should be applied in the assessment of the LOD as far as substances are concerned for which the lead laboratory was asked to provide the ND level.

Determination of LOD/LOQ

Substance	**according to DIN 32645**		**based on signal/noise ratio**	
	LOD µg/100ml H_2O	**LOQ µg/100ml H_2O**	**LOD µg/100ml H_2O**	**LOQ µg/100ml H_2O**
Tributyl citrate	1,73	6,16	1,78	5,36
Tributyl *O*-acetyl citrate	1,45	5,18	0,2	0,6
Triethyl citrate	1,35	4,85	1,2	3,6
Triethyl *O*-acetyl citrate	1,74	6,21	0,12	0,36
Bis(2-ethylhexyl) adipate	1,92	6,83	0,035	0,105
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,69	6,04	0,3	0,9
Bis(2-butoxyethyl) adipate	2	7,13	0,088	0,265
Dioctyl adipate	1,69	6,02	0,094	0,28
Diisodecyl adipate	1,47	5,27	3,12	9,36
Bis(2-ethylhexyl) azelate	1,53	5,46	0,176	0,53
Bis(2-ethylhexyl) sebacate	1,36	4,84	0,17	0,51
Butyl benzoate	1,89	6,75	0,043	0,128
Di(ethylene glycol) dibenzoate	1,44	5,14	0,037	0,11
Di(propylene glycol) dibenzoate	1,47	5,25	0,12	0,36
Tributyl phosphate	1,69	6,04	0,0375	0,113
Triphenyl phosphate	0,092	0,33	0,15	0,45
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0,096	0,34	0,46	1,39
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	0,099	0,35	0,15	0,45
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	0,13	0,46	0,12	0,36
Bis(2-ethylhexyl) phthalate	0,11	0,39	0,033	0,1
Diisononyl phthalate	0,19	0,7	1,76	5,29

From the table follows that the LOQ based on peak/noise 9:1 is about 1,4µg/100ml H_2O for tri-*o*-tolyl phosphate and about 0,4 µg/100ml H_2O for the other two tritolyl phosphates and triphenyl phosphate. To be on the safe side the LOQ was assumed to be 3µg/100ml H_2O (=0,3µg/ml solvent) for all 4 plasticizers for which the ND limit is to be determined. The corresponding LOD is 1µg/100ml H_2O (0,1µg/ml solvent).

5.2 Results of validation

5.2.1 Precision

Precision at 25% of limit

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Tributyl citrate	34,602	0,59	1,71
Tributyl *O*-acetyl citrate	38,26	1,23	3,20
Triethyl citrate	36,03	1,33	3,68
Triethyl *O*-acetyl citrate	38,88	0,45	1,16
Bis(2-ethylhexyl) adipate	39,9	1,60	4,02
Bis[2-(2-butoxyethoxy)ethyl] adipate	35,44	0,54	1,53
Bis(2-butoxyethyl) adipate	38,72	0,93	2,39
Dioctyl adipate	39,26	1,21	3,09
Diisodecyl adipate	39,016	1,86	4,78
Bis(2-ethylhexyl) azelate	40,94	0,90	2,20
Bis(2-ethylhexyl) sebacate	41,58	0,73	1,75
Butyl benzoate	52,5	2,23	4,25
Di(ethylene glycol) dibenzoate	38,06	0,43	1,12
Di(propylene glycol) dibenzoate	37,44	1,77	4,72
Tributyl phosphate	37,676	1,45	3,84
Bis(2-ethylhexyl) phthalate	2,896	0,12	4,16
Diisononyl phthalate	11,43	0,64	5,56

Precision at 1x LOQ

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Triphenyl phosphate	2,686	0,12	4,62
Tri-*o*-tolyl phosphate	2,978	0,18	5,88
Tri-*m*-tolyl phosphate	2,564	0,13	4,97
Tri-*p*-tolyl phosphate	2,852	0,10	3,66

Precision at 50% of limit

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Tributyl citrate	73,84	1,88	2,55
Tributyl *O*-acetyl citrate	73,84	2,21	2,99
Triethyl citrate	68,4	1,23	1,81
Triethyl *O*-acetyl citrate	76	3,11	4,09
Bis(2-ethylhexyl) adipate	73,14	1,89	2,58
Bis[2-(2-butoxyethoxy)ethyl] adipate	82,24	1,10	1,34
Bis(2-butoxyethyl) adipate	73,66	3,64	4,94
Dioctyl adipate	76	1,96	2,57
Diisodecyl adipate	77,56	1,90	2,45
Bis(2-ethylhexyl) azelate	78,378	1,61	2,05
Bis(2-ethylhexyl) sebacate	82,2	3,07	3,73
Butyl benzoate	109,24	2,55	2,34
Di(ethylene glycol) dibenzoate	78,68	2,03	2,58
Di(propylene glycol) dibenzoate	75,84	2,28	3,00
Tributyl phosphate	76,1	1,96	2,58
Bis(2-ethylhexyl) phthalate	5,5	0,34	6,17
Diisononyl phthalate	23,282	0,61	2,60

Precision at 2x LOQ

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Triphenyl phosphate	4,92	0,22	4,41
Tri-*o*-tolyl phosphate	5,206	0,18	3,42
Tri-*m*-tolyl phosphate	4,728	0,16	3,47
Tri-*p*-tolyl phosphate	4,91	0,11	2,32

Precision at 100% of limit

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Tributyl citrate	150,0	1,49	0,99
Tributyl O-acetyl citrate	172,9	4,95	2,87
Triethyl citrate	138,8	2,43	1,75
Triethyl O-acetyl citrate	158,4	4,34	2,74
Bis(2-ethylhexyl) adipate	154,8	7,22	4,67
Bis[2-(2-butoxyethoxy)ethyl] adipate	163,8	10,43	6,37
Bis(2-butoxyethyl) adipate	167,3	5,38	3,22
Dioctyl adipate	176	6,16	3,50
Diisodecyl adipate	151,18	5,23	3,46
Bis(2-ethylhexyl) azelate	170,8	6,91	4,04
Bis(2-ethylhexyl) sebacate	172,8	5,07	2,93
Butyl benzoate	244	14,47	5,93
Di(ethylene glycol) dibenzoate	172,6	9,34	5,41
Di(propylene glycol) dibenzoate	161,4	4,93	3,05
Tributyl phosphate	157,0	4,91	3,13
Bis-(2-ethylhexyl) phthalate	10,26	0,51	5,00
Diisononyl phthalate	47,064	0,76	1,62

Precision at 4x LOQ

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Triphenyl phosphate	10,3	0,34	3,29
Tri-*o*-tolyl phosphate	9,98	0,53	5,27
Tri-*m*-tolyl phosphate	9,49	0,70	7,34
Tri-*p*-tolyl phosphate	9,72	0,74	7,57

Precision at 150% of limit

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Tributyl citrate	214,57	5,11	2,38
Tributyl O-acetyl citrate	277,67	2,08	0,75
Triethyl citrate	211,17	3,40	1,61
Triethyl O-acetyl citrate	229,33	8,74	3,81
Bis(2-ethylhexyl) adipate	244,33	12,34	5,05
Bis[2-(2-butoxyethoxy)ethyl] adipate	227,00	7,00	3,08
Bis(2-butoxyethyl) adipate	251,00	7,55	3,01
Dioctyl adipate	260,33	18,45	7,09
Diisodecyl adipate	268,67	11,93	4,44
Bis(2-ethylhexyl) azelate	217,67	10,02	4,60
Bis(2-ethylhexyl) sebacate	248,67	10,79	4,34
Butyl benzoate	379,67	8,02	2,11
Di(ethylene glycol) dibenzoate	252,00	7,21	2,86
Di(propylene glycol) dibenzoate	246,00	17,35	7,05
Tributyl phosphate	205,67	4,73	2,30
Bis(2-ethylhexyl) phthalate	17,97	0,55	3,07
Diisononyl phthalate	73,70	1,01	1,38

Precision at 6x LOQ

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Triphenyl phosphate	15,07	0,72	4,80
Tri-*o*-tolyl phosphate	17,07	0,12	0,68
Tri-*m*-tolyl phosphate	14,93	0,57	3,81
Tri-*p*-tolyl phosphate	15,97	0,21	1,30

Precision at 200% of limit

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Tributyl citrate	207,4	7,20	3,47
Tributyl O-acetyl citrate	343	3,54	1,03
Triethyl citrate	269,6	14,08	5,22
Triethyl O-acetyl citrate	339,6	9,13	2,69
Bis(2-ethylhexyl) adipate	352,2	26,47	7,52
Bis[2-(2-butoxyethoxy)ethyl] adipate	346,6	14,50	4,18
Bis(2-butoxyethyl) adipate	359	15,57	4,34
Dioctyl adipate	346,2	18,03	5,21
Diisodecyl adipate	355,8	14,24	4,00
Bis(2-ethylhexyl) azelate	353	14,75	4,18
Bis(2-ethylhexyl) sebacate	342	13,78	4,03
Butyl benzoate	492,2	15,99	3,25
Di(ethylene glycol) dibenzoate	367,4	7,80	2,12
Di(propylene glycol) dibenzoate	323	14,80	4,58
Tributyl phosphate	284,8	9,78	3,43
Bis-(2-ethylhexyl) phthalate	25,78	0,51	1,97
Diisononyl phthalate	95,78	1,14	1,19

Precision at 8x LOQ

Component	**Mean**	**S_r**	**RSD_r**
	[µg/100ml H_2O]	[µg/100ml H_2O]	[%]
Triphenyl phosphate	22	0,45	2,03
Tri-*o*-tolyl phosphate	23,46	0,78	3,32
Tri-*m*-tolyl phosphate	20,16	0,38	1,91
Tri-*p*-tolyl phosphate	21,38	1,11	5,21

According to document CEN/TC 52/WG 9/TG 2 N68 Rev.4 the relative standard deviation should be below the limits given in Annex A of this document, which is:

21% for a concentration of 0,01µg/g (=1µg/100ml H_2O)

15% for a concentration of 0,1µg/g (=10µg/100ml H_2O)

11% for a concentration of 1µg/g (=100µg/100ml H_2O)

All measured values are in compliance with these limits.

5.2.2 Recovery

Recovery at 25% - 200% of limit

Component	25% of limit	50% of limit	100% of limit	150% of limit	200% of limit
	%	%	%	%	%
Tributyl citrate	81,4	86,9	88,2	85,1	80,0
Tributyl O-acetyl citrate	90,0	86,9	101,7	108,1	100,9
Triethyl citrate	84,8	80,5	81,6	82,1	79,3
Triethyl O-acetyl citrate	91,5	89,4	93,2	90,1	99,9
Bis(2-ethylhexyl) adipate	93,9	86,0	91,1	97,3	103,6
Bis[2-(2-butoxyethoxy)ethyl] adipate	83,4	96,8	96,4	88,6	101,9
Bis(2-butoxyethyl) adipate	91,1	86,7	98,4	94,5	105,6
Dioctyl adipate	92,4	89,4	103,5	101,7	101,8
Diisodecyl adipate	91,8	91,2	88,9	104,5	104,6
Bis(2-ethylhexyl) azelate	96,3	92,2	100,5	84,3	103,8
Bis(2-ethylhexyl) sebacate	97,8	96,7	101,6	97,7	100,6
Butyl benzoate	88,6	88,1	98,4	100,6	99,2
Di(ethylene glycol) dibenzoate	89,6	92,6	101,5	100,1	108,1
Di(propylene glycol) dibenzoate	88,1	89,2	94,9	95,6	95,0
Tributyl phosphate	88,6	89,5	92,4	82,4	83,8
Bis-(2-ethylhexyl) phthalate	96,5	91,7	85,5	99,3	107,4
Diisononyl phthalate	91,4	93,1	94,1	97,9	95,8

Recovery at 1x - 8x LOQ

Component	1xLOQ	2xLOQ	4xLOQ	6xLOQ	8xLOQ
	%	%	%	%	%
Triphenyl phosphate	89,5	82,0	85,8	82,8	91,7
Tri-*o*-tolyl phosphate	99,3	86,8	83,2	93,9	97,8
Tri-*m*-tolyl phosphate	85,5	78,8	79,1	84,4	84,0
Tri-*p*-tolyl phosphate	95,1	81,8	81,0	88,6	89,1

According to document CEN TC 52 WG9 TG2 N68rev4 the recommended recovery targets are:

80-110% for a concentration levels 0,1µg/g to 10µg/g

(=10µg/100ml H_2O to 1000µg/100ml H_2O)

60-115% for 0,01µg/g (=1µg/100ml)

All measured values are in compliance with these limits.

5.2.3 Linearity

Regression line 25% - 200% of limit

Component	Corr. Coefficient(r) linear	Slope (b) resp/ppb	Intercept (a) resp	S_{res} resp
Tributyl citrate	0,9967	9,038	-284	881,1
Tributyl O-acetyl citrate	0,9976	10,491	-561	859,3
Triethyl citrate	0,9979	7,965	210,19	609,8
Triethyl O-acetyl citrate	0,9966	9,769	-555,26	964
Bis(2-ethylhexyl) adipate	0,9960	10,312	-973	1122,7
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,9968	10,118	-573,5	966,7
Bis(2-butoxyethyl) adipate	0,9956	10,415	-758	1164,5
Dioctyl adipate	0,9969	10,337	-444	984,6
Diisodecyl adipate	0,9976	10,545	-670,1	877,6
Bis(2-ethylhexyl) azelate	0,9974	9,648	-20,3	832,6
Bis(2-ethylhexyl) sebacate	0,9980	10,008	-84,2	764,8
Butyl benzoate	0,9981	10,135	-806,75	1079
Di(ethylene glycol) dibenzoate	0,9977	10,664	-748,8	865,9
Di(propylene glycol) dibenzoate	0,9976	9,617	-304	797
Tributyl phosphate	0,9968	8,253	539,65	788
Bis(2-ethylhexyl) phthalate	0,9972	10,666	-56	66,5
Diisononyl phthalate	0,9995	9,685	-56,6	106,5

Regression line 1x – 8x LOQ

Component	Corr. Coefficient(r) linear	Slope (b) resp/ppb	Intercept (a) resp	S_{res} resp
Triphenyl phosphate	0,9981	10,374	-27,7	46,7
Tri-*o*-tolyl phosphate	0,9978	9,366	-22,4	49,2
Tri-*m*-tolyl phosphate	0,9978	8,277	-1,17	46,3
Tri-*p*-tolyl phosphate	0,9962	8,867	-16,9	65,3

The correlation coefficient r is better than 0,995 for all plasticizers.

5.2.4 Limit of Detection (LOD) / Limit of Quantification (LOQ)

The validation confirmed the estimated LOQ levels for those substances for which the lead laboratory was asked to provide LOD/LOQ levels, i.e. LOD 1µg/100ml H_2O and LOQ 3µg/100ml H_2O corresponding to LOD 0,1 µg/ml solvent and LOQ 0,3 µg/ml solvent for triphenyl, tri-*o*-tolyl, tri-*m*-toyl and tri-*p*-tolyl phosphate.

LOD/LOQs are tabulated in 5.1.

5.2.5 Stability of standard solutions

After 3 months of storage of the stock solution at room temperature no decrease of the plasticizer concentrations could be observed. In addition, no degradation products could be found.

After 4 weeks of storage of the calibration standard solutions no concentration changes could be detected.

6 Peer Review

The Peer Review was performed by:

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The reports can be found in Annex C.

In the following a comparison of the data is presented. AIJU found that some of the recovery data did not comply with the agreed acceptance criteria and were below the 80% required for these substances in the relevant concentrations (between 70% and 80%). It should be noted that AIJU used a concentration which was a factor of 10 higher compared to the other labs for some substances (butyl benzoate and the dibenzoates) which may have influenced the results. All data from LGA were in compliance with the acceptance criteria.

LOD/LOQ based on signal/noise ratio

Substance	**LOD µg/100ml H_2O**			**LOQ µg/100ml H_2O**		
	Fiala Steiner	**AIJU**	**LGA**	**Fiala Steiner**	**AIJU**	**LGA**
Tributyl citrate	1,78	0.8	1,71	5,36	2.4	5,12
Tributyl *O*-acetyl citrate	0,2	0.4	0,21	0,6	1.2	0,63
Triethyl citrate	1,2	0.4	1,15	3,6	1.2	3,45
Triethyl *O*-acetyl citrate	0,12	0.2	0,14	0,36	0.6	0,42
Bis(2-ethylhexyl) adipate	0,035	0.9	0,04	0,105	2.7	0,12
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,3	1.1	0,29	0,9	3.3	0,87
Bis(2-butoxyethyl) adipate	0,088	0.8	0,09	0,265	2.4	0,27
Dioctyl adipate	0,094	0.3	0,11	0,28	0.9	0,33
Diisodecyl adipate	3,12	3.0	3,02	9,36	9.0	9,06
Bis(2-ethylhexyl) azelate	0,176	0.9	0,17	0,53	2.7	0,51
Bis(2-ethylhexyl) sebacate	0,17	1.2	0,15	0,51	3.6	0,45
Butyl benzoate*	0,043	0.1	0,05	0,128	0.3	0,15
Di(ethylene glycol) dibenzoate*	0,037	0.3	0,03	0,11	0.9	0,09
Di(propylene glycol) dibenzoate*	0,12	0.2	0,13	0,36	0.6	0,39
Tributyl phosphate	0,0375	1.3	0,04	0,113	3.9	0,12
Triphenyl phosphate	0,15	0.3	0,16	0,45	0.9	0,48
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0,46	0.6	0,51	1,39	1.8	1,53
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	0,15	1.2	0,16	0,45	3.6	0,48
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	0,12	1.5	0,12	0,36	4.5	0,36
Bis(2-ethylhexyl) phthalate	0,033	0.6	0,04	0,1	1.8	0,12
Diisononyl phthalate	1,76	0.8	1,90	5,29	2.4	5,70

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 25% of limit

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	1,71	8.9	3,51
Tributyl *O*-acetyl citrate	3,20	1.3	1,05
Triethyl citrate	3,68	2.0	5,15
Triethyl *O*-acetyl citrate	1,16	2.5	2,45
Bis(2-ethylhexyl) adipate	4,02	5.1	7,65
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,53	4.7	4,22
Bis(2-butoxyethyl) adipate	2,39	7.5	4,53
Dioctyl adipate	3,09	2.4	5,15
Diisodecyl adipate	4,78	6.1	4,20
Bis(2-ethylhexyl) azelate	2,20	2.1	4,15
Bis(2-ethylhexyl) sebacate	1,75	6.5	3,91
Butyl benzoate*	4,25	2.6	3,10
Di(ethylene glycol) dibenzoate*	1,12	5.2	2,29
Di(propylene glycol) dibenzoate*	4,72	3.9	4,66
Tributyl phosphate	3,84	3.2	3,46
Bis(2-ethylhexyl) phthalate	4,16	9.4	2,02
Diisononyl phthalate	5,56	6.0	1,07

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 1x LOQ

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	4,62	5.6	4,91
Tri-*o*-tolyl phosphate	5,88	4.8	5,36
Tri-*m*-tolyl phosphate	4,97	1.8	3,43
Tri-*p*-tolyl phosphate	3,66	2.9	6,45

Precision at 50% of limit

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	2,55	4.5	2,75
Tributyl *O*-acetyl citrate	2,99	3.9	3,22
Triethyl citrate	1,81	3.7	3,79
Triethyl *O*-acetyl citrate	4,09	9.0	3,10
Bis(2-ethylhexyl) adipate	2,58	3.5	4,12
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,34	5.2	4,66
Bis(2-butoxyethyl) adipate	4,94	3.5	2,26
Dioctyl adipate	2,57	4.2	3,15
Diisodecyl adipate	2,45	3.6	4,85
Bis(2-ethylhexyl) azelate	2,05	2.7	2,24
Bis(2-ethylhexyl) sebacate	3,73	3.3	2,69
Butyl benzoate*	2,34	2.9	4,12
Di(ethylene glycol) dibenzoate*	2,58	2.3	3,15
Di(propylene glycol) dibenzoate*	3,00	3.2	4,85
Tributyl phosphate	2,58	2.8	4,91
Bis(2-ethylhexyl) phthalate	6,17	5.2	4,25
Diisononyl phthalate	2,60	3.1	5,69

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 2x LOQ

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	4,41	6.9	4,80
Tri-*o*-tolyl phosphate	3,42	6.7	5,67
Tri-*m*-tolyl phosphate	3,47	6.2	5,21
Tri-*p*-tolyl phosphate	2,32	5.8	5,02

Precision at 100% of limit

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	0,99	3.5	4,61
Tributyl *O*-acetyl citrate	2,87	4.4	3,94
Triethyl citrate	1,75	3.6	3,90
Triethyl *O*-acetyl citrate	2,74	7.1	4,15
Bis(2-ethylhexyl) adipate	4,67	6.9	2,66
Bis[2-(2-butoxyethoxy)ethyl] adipate	6,37	5.4	2,44
Bis(2-butoxyethyl) adipate	3,22	2.9	5,10
Dioctyl adipate	3,50	3.2	2,69
Diisodecyl adipate	3,46	2.7	2,54
Bis(2-ethylhexyl) azelate	4,04	3.6	2,15
Bis(2-ethylhexyl) sebacate	2,93	3.1	3,86
Butyl benzoate*	5,93	5.8	2,44
Di(ethylene glycol) dibenzoate*	5,41	2.9	2,68
Di(propylene glycol) dibenzoate*	3,05	2.8	3,05
Tributyl phosphate	3,13	4.9	2,63
Bis(2-ethylhexyl) phthalate	5,00	4.1	5,96
Diisononyl phthalate	1,62	3.5	2,43

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 4x LOQ

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	3,29	3.7	5,60
Tri-*o*-tolyl phosphate	5,27	4.2	4,91
Tri-*m*-tolyl phosphate	7,34	5.3	3,85
Tri-*p*-tolyl phosphate	7,57	6.6	3,69

Precision at 150% of limit

	RSD$_r$ [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	2,38	0.4	2,05
Tributyl *O*-acetyl citrate	0,75	5.8	3,86
Triethyl citrate	1,61	4.9	2,85
Triethyl *O*-acetyl citrate	3,81	1.7	2,46
Bis(2-ethylhexyl) adipate	5,05	2.1	5,02
Bis[2-(2-butoxyethoxy)ethyl] adipate	3,08	4.3	6,28
Bis(2-butoxyethyl) adipate	3,01	7.6	3,52
Dioctyl adipate	7,09	1.5	3,69
Diisodecyl adipate	4,44	1.9	3,51
Bis(2-ethylhexyl) azelate	4,60	2.8	4,01
Bis(2-ethylhexyl) sebacate	4,34	2.2	3,02
Butyl benzoate*	2,11	4.2	5,83
Di(ethylene glycol) dibenzoate*	2,86	1.8	5,19
Di(propylene glycol) dibenzoate*	7,05	1.5	3,15
Tributyl phosphate	2,30	2.2	3,21
Bis(2-ethylhexyl) phthalate	3,07	5.4	4,89
Diisononyl phthalate	1,38	1.7	3,26

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 6x LOQ

	RSD$_r$ [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	4,80	4.7	3,02
Tri-*o*-tolyl phosphate	0,68	6.1	3,31
Tri-*m*-tolyl phosphate	3,81	2.5	3,29
Tri-*p*-tolyl phosphate	1,30	4.3	3,01

Precision at 200% of limit

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	3,47	1.8	4,51
Tributyl *O*-acetyl citrate	1,03	1.7	2,05
Triethyl citrate	5,22	4.6	4,15
Triethyl *O*-acetyl citrate	2,69	3.1	2,45
Bis(2-ethylhexyl) adipate	7,52	5.3	5,65
Bis[2-(2-butoxyethoxy)ethyl] adipate	4,18	5.8	3,22
Bis(2-butoxyethyl) adipate	4,34	1.7	3,53
Dioctyl adipate	5,21	2.5	4,15
Diisodecyl adipate	4,00	2.3	4,20
Bis(2-ethylhexyl) azelate	4,18	3.8	4,15
Bis(2-ethylhexyl) sebacate	4,03	2.6	3,91
Butyl benzoate*	3,25	1.7	3,10
Di(ethylene glycol) dibenzoate*	2,12	5.6	2,29
Di(propylene glycol) dibenzoate*	4,58	2.5	4,66
Tributyl phosphate	3,43	3.3	2,46
Bis(2-ethylhexyl) phthalate	1,97	2.9	2,02
Diisononyl phthalate	1,19	2.5	1,57

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Precision at 8x LOQ

	RSD_r [%]		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	2,03	2.1	2,51
Tri-*o*-tolyl phosphate	3,32	2.6	2,99
Tri-*m*-tolyl phosphate	1,91	5.8	2,43
Tri-*p*-tolyl phosphate	5,21	3.6	3,45

Recovery at 25% - 200% of limit, non-complying values in red and underlined

		Recovery %				
Component		**25% of limit**	**50% of limit**	**100% of limit**	**150% of limit**	**200% of limit**
Tributyl citrate	Fiala/Steiner	81,4	86,9	88,2	85,1	80,0
	AIJU	75.5	77.4	83.2	93.4	101.7
	LGA	81	82	85	84	85
Tributyl O-acetyl citrate	Fiala/Steiner	90,0	86,9	101,7	108,1	100,9
	AIJU	79.6	102.3	86.4	89.5	102.0
	LGA	92	91	95	99	98
Triethyl citrate	Fiala/Steiner	84,8	80,5	81,6	82,1	79,3
	AIJU	91.9	86.0	98.9	82.8	89.3
	LGA	80	83	81	84	83
Triethyl O-acetyl citrate	Fiala/Steiner	91,5	89,4	93,2	90,1	99,9
	AIJU	91.8	82.0	100.4	98.2	99.3
	LGA	91	95	92	96	97
Bis(2-ethylhexyl) adipate	Fiala/Steiner	93,9	86,0	91,1	97,3	103,6
	AIJU	72.1	71.9	77.4	88.3	96.6
	LGA	95	89	92	98	99
Bis[2-(2-butoxyethoxy)ethyl] adipate	Fiala/Steiner	83,4	96,8	96,4	88,6	101,9
	AIJU	83.0	77.2	97.1	99.0	99.3
	LGA	86	91	96	89	102
Bis(2-butoxyethyl) adipate	Fiala/Steiner	91,1	86,7	98,4	94,5	105,6
	AIJU	74.7	78.1	89.6	99.9	101.2
	LGA	89	88	98	97	95
Dioctyl adipate	Fiala/Steiner	92,4	89,4	103,5	101,7	101,8
	AIJU	89.7	72.5	97.2	96.5	83.2
	LGA	95	90	102	105	98
Diisodecyl adipate	Fiala/Steiner	91,8	91,2	88,9	104,5	104,6
	AIJU	82.6	71.0	99.2	93.7	86.7
	LGA	95	91	96	103	99
Bis(2-ethylhexyl) azelate	Fiala/Steiner	96,3	92,2	100,5	84,3	103,8
	AIJU	76.2	77.8	85.2	82.1	94.1
	LGA	98	90	99	88	102
Bis(2-ethylhexyl) sebacate	Fiala/Steiner	97,8	96,7	101,6	97,7	100,6
	AIJU	94.5	97.8	84.8	98.7	77.8
	LGA	95	97	101	99	100

Butyl benzoate*	Fiala/Steiner	88,6	88,1	98,4	100,6	99,2
	AIJU	91.5	97.7	91.1	100.4	98.5
	LGA	87	88	95	98	97
Di(ethylene glycol) dibenzoate*	Fiala/Steiner	89,6	92,6	101,5	100,1	108,1
	AIJU	80.3	82.6	76.4	81.3	99.2
	LGA	91	89	104	101	98
Di(propylene glycol) dibenzoate*	Fiala/Steiner	88,1	89,2	94,9	95,6	95,0
	AIJU	99.4	83.1	81.0	92.4	100.0
	LGA	89	90	95	94	93
Tributyl phosphate	Fiala/Steiner	88,6	89,5	92,4	82,4	83,8
	AIJU	92.2	89.2	78.3	96.5	93.1
	LGA	92	89	93	95	88
Bis-(2-ethylhexyl) phthalate	Fiala/Steiner	96,5	91,7	85,5	99,3	107,4
	AIJU	88.2	102.2	103.9	92.7	95.1
	LGA	99	98	88	101	104
Diisononyl phthalate	Fiala/Steiner	91,4	93,1	94,1	97,9	95,8
	AIJU	87.8	101.4	98.7	101.7	105.2
	LGA	90	88	93	99	95

* AIJU used a concentration which was 10x higher compared to the other labs for the indicated substances.

Recovery at 1x - 8x LOQ

		Recovery %				
Component		**1xLOQ**	**2xLOQ**	**4xLOQ**	**6xLOQ**	**8xLOQ**
Triphenyl phosphate	Fiala/Steiner	89,5	82,0	85,8	82,8	91,7
	AIJU	95.2	96.7	93.0	99.4	99.0
	LGA	88	83	89	87	93
Tri-*o*-tolyl phosphate	Fiala/Steiner	99,3	86,8	83,2	93,9	97,8
	AIJU	89.4	100.6	80.1	91.4	88.0
	LGA	101	89	86	91	99
Tri-*m*-tolyl phosphate	Fiala/Steiner	85,5	78,8	79,1	84,4	84,0
	AIJU	98.3	96.8	90.2	98.9	101.6
	LGA	82	81	85	89	86
Tri-*p*-tolyl phosphate	Fiala/Steiner	95,1	81,8	81,0	88,6	89,1
	AIJU	93.0	106.7	99.7	94.2	99.5
	LGA	85	89	90	91	86

Regression line 25% - 200% of limit

	Corr. Coefficient(r) linear		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Tributyl citrate	0,9967	0,9998	0,9972
Tributyl O-acetyl citrate	0,9976	0,9963	0,9953
Triethyl citrate	0,9979	0,9989	0,9960
Triethyl O-acetyl citrate	0,9966	0,9995	0,9981
Bis(2-ethylhexyl) adipate	0,9960	0,9997	0,9956
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,9968	0,9977	0,9975
Bis(2-butoxyethyl) adipate	0,9956	0,9976	0,9980
Dioctyl adipate	0,9969	0,9986	0,9977
Diisodecyl adipate	0,9976	0,9991	0,9986
Bis(2-ethylhexyl) azelate	0,9974	0,9961	0,9955
Bis(2-ethylhexyl) sebacate	0,9980	0,9991	0,9965
Butyl benzoate*	0,9981	0,9975	0,9979
Di(ethylene glycol) dibenzoate*	0,9977	0,9981	0,9960
Di(propylene glycol) dibenzoate*	0,9976	0,9986	0,9958
Tributyl phosphate	0,9968	0,9999	0,9956
Bis(2-ethylhexyl) phthalate	0,9972	0,9992	0,9985
Diisononyl phthalate	0,9995	0,9974	0,9958

Regression line 1x – 8x LOQ

	Corr. Coefficient(r) linear		
Component	**Fiala/Steiner**	**AIJU**	**LGA**
Triphenyl phosphate	0,9981	0,9985	0,9976
Tri-*o*-tolyl phosphate	0,9978	0,9985	0,9974
Tri-*m*-tolyl phosphate	0,9978	0,9993	0,9975
Tri-*p*-tolyl phosphate	0,9962	0,9985	0,9961

7 SOP and Normative requirements

Annex B of this report contains a Standard Operation Procedure (SOP) for all 21 plasticizers included in the method development, validation and Peer Review (SOP for priority 1 and 2 plasticizers).

In addition, Annex D includes a slightly simplified procedure which covers only 4 chemicals (Normative requirements for priority 1 plasticizers):

- Triphenyl phosphate
- Tri-*o*-tolyl phosphate
- Tri-*m*-tolyl phosphate
- Tri-*p*-tolyl phosphate

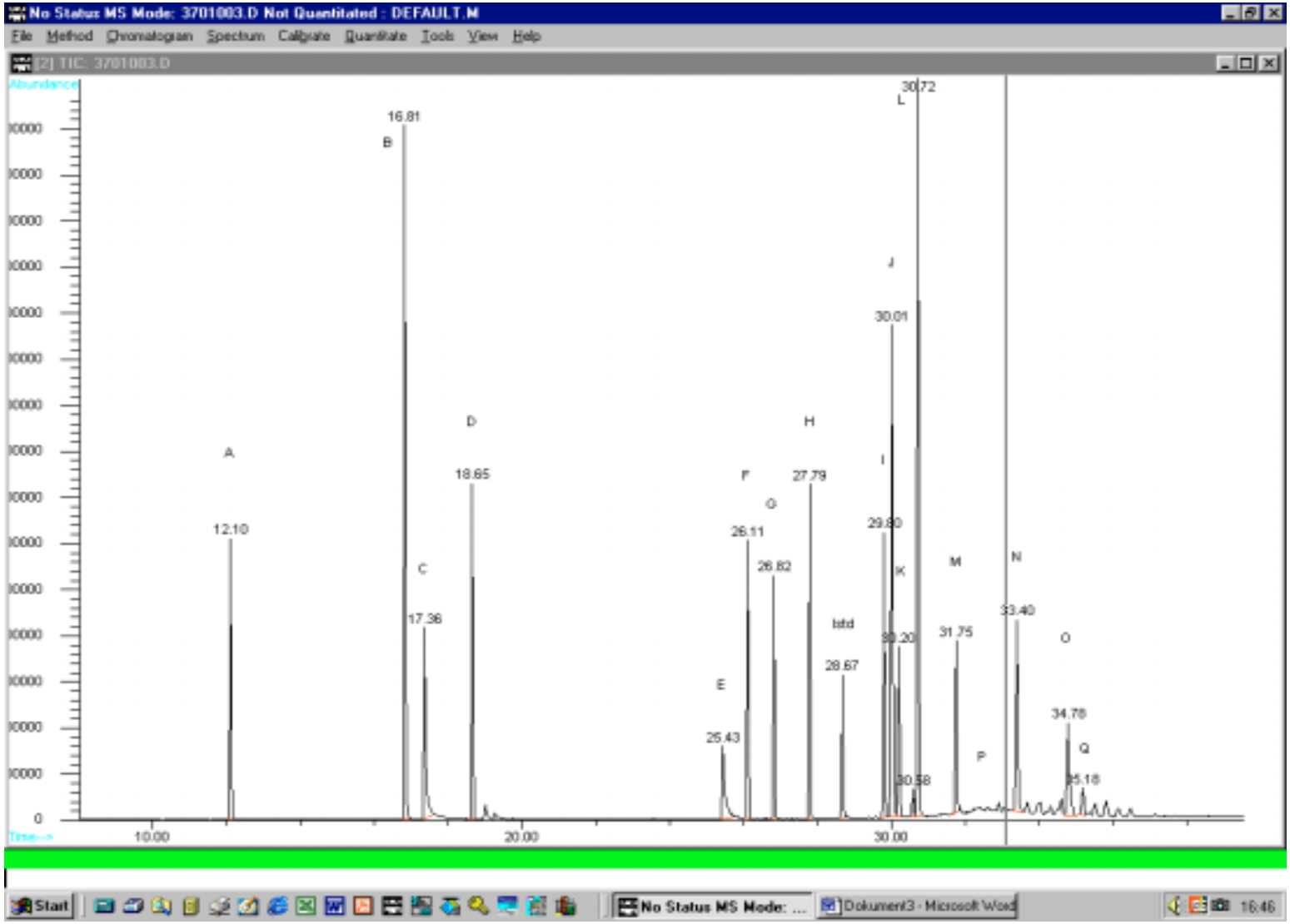
The first edition of the European standard dealing with organic chemicals in toys will cover only these plasticizers. The procedure described in Annex D is intended to be inserted in the draft standard.

8 Literature search

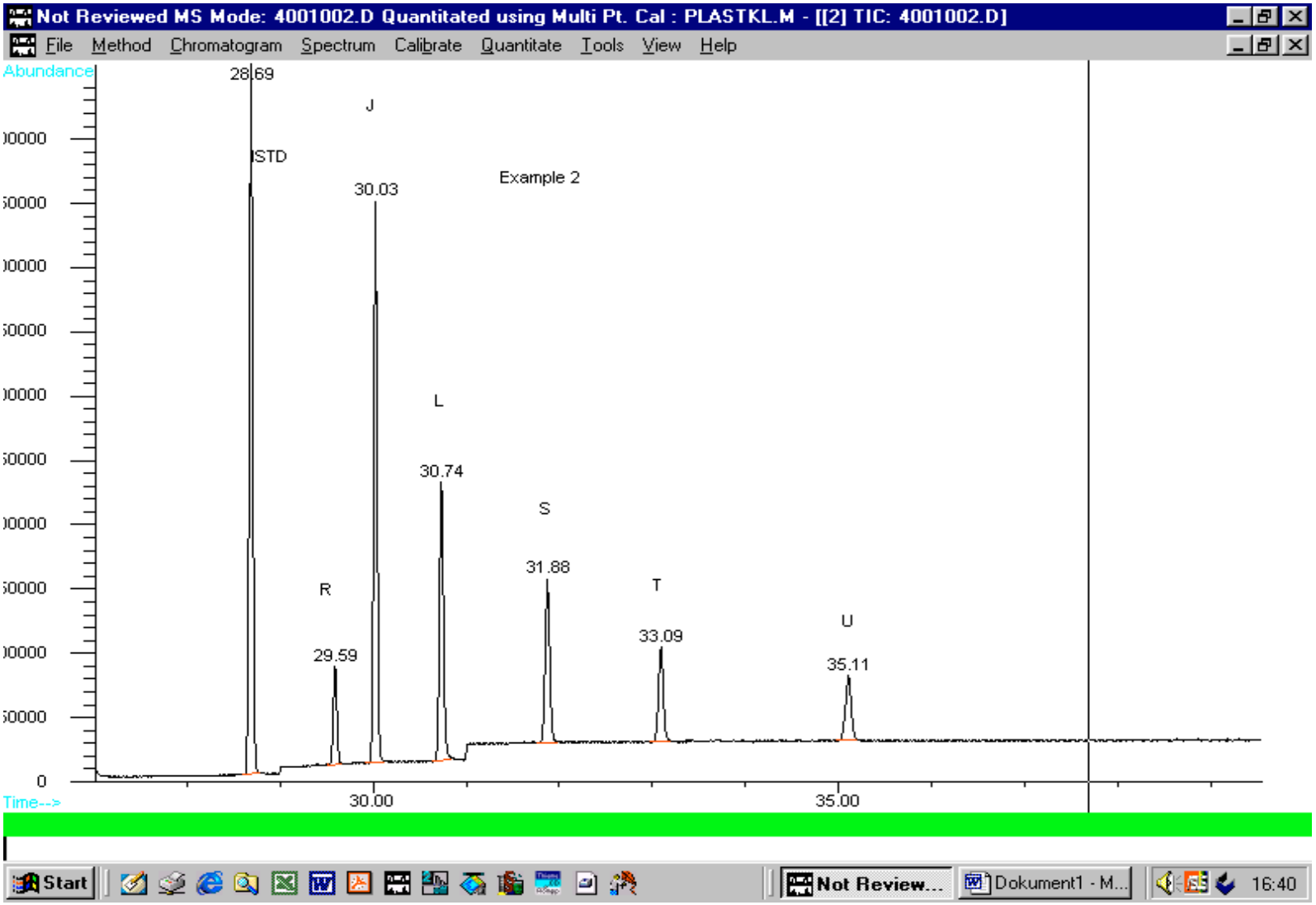
A literature study was carried out in preparation of the method development. It can be found in Annex E.

Annex A Chromatograms of plasticizers

Letter in chromatogram	Substance	CAS Number
A	Butyl benzoate	136-60-7
B	Tributyl phosphate	126-73-8
C	Triethyl citrate	77-93-0
D	Triethyl *O*-acetyl citrate	77-89-4
E	Tributyl citrate	77-94-1
F	Tributyl *O*-acetyl citrate	77-90-7
G	Bis(2-butoxyethyl) adipate	141-18-4
H	Bis(2-ethylhexyl) adipate	103-23-1
I	Dioctyl adipate	123-79-5
J	Bis (2-ethylhexyl) phthalate	117-81-7
K	Di(propylene glycol) dibenzoate	94-51-9
L	Di(ethylene glycol) dibenzoate	120-55-8
M	Bis(2-ethylhexyl) azelate	103-24-2
N	Bis(2-ethylhexyl) sebacate	122-62-3
O	Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3
P	Diisodecyl adipate	27178-16-1
Q	Diisononyl phthalate	68515-48-0
R	Triphenyl phosphate	115-86-6
S	Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8
T	Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2
U	Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0



Chromatogram of plasticizers - program A - screenshot



Chromatogram of plasticizers – program B - screenshot

Annex B SOP for priority 1 and 2 plasticizers

1. Scope

This method describes the analysis of plasticizers in aqueous solution (obtained by extraction of toy samples with water) using liquid/liquid extraction and GC/MS analysis. The plasticizers as well as the validated concentration ranges are indicated in the table below.

Substance	**CAS**	**in 100ml H_2O**
Tributyl citrate	77-94-1	42,5 - 340µg
Tributyl *O*-acetyl citrate	77-90-7	42,5 - 340µg
Triethyl citrate	77-93-0	42,5 - 340µg
Triethyl *O*-acetyl citrate	77-89-4	42,5 - 340µg
Bis(2-ethylhexyl) adipate	103-23-1	25,0 - 200µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	42,5 - 340µg
Bis(2-butoxyethyl) adipate	141-18-4	42,5 - 340µg
Dioctyl adipate	123-79-5	42,5 - 340µg
Diisodecyl adipate	27178-16-1	42,5 - 340µg
Bis(2-ethylhexyl) azelate	103-24-2	42,5 - 340µg
Bis(2-ethylhexyl) sebacate	122-62-3	42,5 - 340µg
Butyl benzoate	136-60-7	42,5 - 340µg as benzoic acid
Di(ethylene glycol) dibenzoate	120-55-8	42,5 - 340µg
Di(propylene glycol) dibenzoate	94-51-9	42,5 - 340µg
Tributyl phosphate	126-73-8	42,5 - 340µg
Triphenyl phosphate	115-86-6	3,0 - 24µg
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	3,0 - 24µg
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	3,0 - 24µg
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	3,0 - 24µg
Bis(2-ethylhexyl) phthalate	117-81-7	3,0 - 24µg
Diisononyl phthalate	68515-48-0	12,5 - 100µg

2. Principle

An aqueous solution of plasticizers is subjected to a single extraction using toluene:ethylacetate 95:5 in a separatory funnel. The concentrations are determined by GC/MS in SIM-mode using a non-polar column. For quantification both external and internal standards are used.

3. Chemicals

3.1 Solvents

3.1.1

Acetone analytical grade or equivalent

3.1.2

Toluene analytical grade or equivalent

3.1.3

Ethylacetate analytical grade or equivalent

3.1.4

Solvent Mixture: Mixture containing 95%-vol toluene and 5%-vol ethylacetate

3.1.5

Water deionized, PH 6-8

3.2 Plasticizers

Substance	Purity according to manuf.	CAS-Nr.	Manufacturer
Tributyl citrate	>99%	77-94-1	Merck
Tributyl O-acetyl citrate	>99.0%	77-90-7	Fluka
Triethyl citrate	>98%	77-93-0	Fluka
Triethyl O-acetyl citrate	>99.0%	77-89-4	Fluka
Bis(2-ethylhexyl) adipate	>99%	103-23-1	Fluka
Bis[2-(2-butoxyethoxy)ethyl] adipate	?	141-17-3	Aldrich
Bis(2-butoxyethyl) adipate	Techn.	141-18-4	Aldrich
Dioctyl adipate	?	123-79-5	Chem Service
Diisodecyl adipate	Techn.	27178-16-1	Aldrich
Bis(2-ethylhexyl) azelate	Ca. 80%	103-24-2	Merck
Bis(2-ethylhexyl) sebacate	>97%	122-62-3	Fluka
Butyl benzoate	>98%	136-60-7	Fluka

Di(ethylene glycol) dibenzoate	96%	120-55-8	Aldrich
Di(propylene glycol) dibenzoate	?	94-51-9	Chem Service
Tributyl phosphate	p.A. >99%	126-73-8	Merck
Triphenyl phosphate	>98%	115-86-6	Fluka
Tri-*o*-tolyl phosphate	98%	78-30-8	Chem Service
Tri-*m*-tolyl phosphate	97%	563-04-2	Acros
Tri-*p*-tolyl phosphate	>98%	78-32-0	Acros
Bis(2-ethylhexyl) phthalate	> 97%	117-81-7	Fluka
Diisononyl phthalate	techn.	68515-48-0	Fluka

or equivalent from other producers

3.3 Other

3.3.1

Benzylbutyl phthalate (internal standard)

4. Apparatus

Gaschromatograph: HP5890 Series II or equivalent

Analytical column: Optima delta-3 (manufacturer: Macherey & Nagel, Germany), dimensions: 30m*0,25mm*0,25µm, or equivalent

Autoinjector: HP7673A equipped with a 10µl syringe fast injection mode or equivalent (or handheld syringe)
Split/Splitless-injector at constant pressure or equivalent, split flow 10ml/min, split injection
Injection volume: 1µl
Pressure: 150kPa Helium (Purity: 99,999% or better)
Septum purge flow: 2ml/min
Inlet temp.: 275°C

Oven temp. progr.: Init Temp.: 100°C
Init Time: 1min
Rate: 7°C/min
Final Temp.: 300°C
Final Time: 10min

Slight deviations are acceptable provided the peak resolution is sufficient (Rs $\geq$ 1,5)

Transfer-Line Temp.: 290°C

Mass selective Detector: HP5970B or equivalent

Software: G1701AA Rel. A03.00 or equivalent for data processing

Single Ion monitoring: For each substance two ions are used for quantification: typically the base ion as target ion and the ion with the second highest peak in the mass spectrum as qualifier. In the case of interference with other substances other ions are chosen. The target ion is used for quantification, the qualifying ion is used for positive identification of the substance. The use of a qualifier ion reduces the risk of false positive results due to interfering signals. A deviation of 20% from the expected response of the qualifier ion is acceptable.

List of target and qualifier ions for plasticizers:

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Tributyl citrate	77-94-1	129	185
Tributyl *O*-acetyl citrate	77-90-7	185	129
Triethyl citrate	77-93-0	157	115
Triethyl *O*-acetyl citrate	77-89-4	157	203
Bis(2-ethylhexyl) adipate	103-23-1	129	111
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	99	85
Bis(2-butoxyethyl) adipate	141-18-4	85	111
Dioctyl adipate	123-79-5	129	241
Diisodecyl adipate	27178-16-1	129	111
Bis(2-ethylhexyl) azelate	103-24-2	171	112
Bis(2-ethylhexyl) sebacate	122-62-3	185	112
Butyl benzoate	136-60-7	105	123
Di(ethylene glycol) dibenzoate	120-55-8	105	149
Di(propylene glycol) dibenzoate	94-51-9	105	163
Tributyl phosphate	126-73-8	99	155
Triphenyl phosphate	115-86-6	325	169
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	165	179
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	368	165
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	368	165
Bis(2-ethylhexyl) phthalate	117-81-7	149	167
Diisononyl phthalate	68515-48-0	149	293

Target and qualifier ions for internal standard

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Benzylbutyl phthalate (Internal Standard)	85-68-7	149	206

Time windows:
Due to interferences two runs using different time windows are required. The first run - program A - covers the internal standard (benzylbutyl phthalate) and all substances except the ones mentioned below for the second run. The second run - program B - covers the internal standard, bis (2-ethylhexyl) phthalate, triphenyl phosphate, tri-*o*-tolyl phosphate, tri-*m*-tolyl phosphate and tri-*p*-tolyl phosphate.

Time windows of monitored ions (Program A):

Start time [min]	Monitored ions [amu]
8	99, 105, 115, 123, 155, 157, 203
24	85, 111, 129, 149, 185
29,3	105, 129, 149, 241
31	85, 99, 111, 112, 129, 149, 171, 293

Time windows of monitored ions (Program B):

Start time [min]	Monitored ions [amu]
27	149, 206
29	149, 167, 325, 169
31	165, 179, 368

Glass separatory funnels 250ml with glass stopper and teflon faucet
Volumometric glassware (pipettes, measuring cylinders, flasks)
Pipette 50µl
Vials for autosampler
Usual laboratory equipment

5. Procedure

5.1 General

Rinse all glass ware and other items in contact with the sample or standard solutions twice with acetone.

5.2 Stock solutions

A stock solution in acetone is prepared containing benzylbutyl phthalate to the nearest of 10mg/ml (Stock solution Istd1). Prepare a dilution 1:10 in acetone to obtain a concentration of 1mg/ml (Stock solution Istd2).

A stock solution in acetone is prepared containing all plasticizers to the nearest of the following concentration levels (Stock solution P):

Substance	**Concentration [mg/ml]**
Triethyl citrate	1,7
Triethyl O-acetyl citrate	1,7
Tributyl citrate	1,7
Tributyl O-acetyl citrate	1,7
Bis(2-ethylhexyl) adipate	1,0
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,7
Bis(2-butoxyethyl) adipate	1,7
Dioctyl adipate	1,7
Diisodecyl adipate	1,7
Bis(2-ethylhexyl) azelate	1,7
Bis(2-ethylhexyl) sebacate	1,7
Butyl benzoate (*)	2,5
Di(ethylene glycol) dibenzoate	1,7
Di(propylene glycol) dibenzoate	1,7
Tributyl phosphate	1,7
Triphenyl phosphate	0,12
Tri-*o*-tolyl phosphate	0,12
Tri-*m*-tolyl phosphate	0,12
Tri-*p*-tolyl phosphate	0,12
Bis(2-ethylhexyl) phthalate	0,12
Diisononyl phthalate	0,5

(*) The concentration of butyl benzoate was chosen to obtain a level of 1,7mg/ml as benzoic acid.

5.3 Calibration standards

Dilute stock solution P to obtain calibration standards at the 200%, 150%, 100%, 50% and 25% level of the concentrations given below. Use toluene as a solvent.

Calibration standard 100%:

Substance	**CAS Number**	**in 1ml toluene**
Tributyl citrate	77-94-1	17µg
Tributyl *O*-acetylcitrate	77-90-7	17µg
Triethyl citrate	77-93-0	17µg
Triethyl *O*-acetylcitrate	77-89-4	17µg
Bis(2-ethylhexyl) adipate	103-23-1	10µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	17µg
Bis(2-butoxyethyl) adipate	141-18-4	17µg
Dioctyl adipate	123-79-5	17µg
Diisodecyl adipate	27178-16-1	17µg
Bis(2-ethylhexyl) azelate	103-24-2	17µg
Bis(2-ethylhexyl) sebacate	122-62-3	17µg
Butyl benzoate	136-60-7	25µg
Di(ethylene glycol) dibenzoate	120-55-8	17µg
Di(propylene glycol) dibenzoate	94-51-9	17µg
Tributyl phosphate	126-73-8	17µg
Triphenyl phosphate	115-86-6	1,2µg
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	1,2µg
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	1,2µg
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	1,2µg
Bis (2-ethylhexyl) phthalate	117-81-7	1,2µg
Diisononyl phthalate	68515-48-0	5µg

Add stock solution Istd (benzylbutyl phthalate in acetone; c=10mg/ml) as internal standard to obtain a internal standard concentration of 5µg/ml. This can be achieved, e.g. by adding 50µl of the stock solution Istd1 to 100ml of the diluted stock solutions.

5.4 Sample extration

Prepare a blank by adding 50µl of stock solution Istd1 of benzylbutyl phthalate in acetone (c=10mg/ml) to 1l of deionized water.

Add 50µl of stock solution Istd2 of benzylbutyl phthalate in acetone (c=1mg/ml) to 100ml water sample.

100ml of the blank or water sample are extracted with 10ml of the solvent mixture containing 95%-vol toluene and 5%-vol ethylacetate by shaking in a 250ml separatory funnel for 1 minute. Let the two phases set apart and draw off the upper layer.

5.5 Analytical determination

Analyse each calibration standard, blank and sample following the conditions defined in clause 4.

After data collection is complete establish calibration curves using the appropriate target and qualifier ions. The internal standard should be used. Correlation coefficient should be better than 0,995 for a linear calibration function. If not, use a 2^{nd} order calibration function.

Determine plasticizer content in the samples by using these calibration curves.

Content of plasticizers determined in blank should not exceed 10% of the content in the lowest calibration standard.

5.6 Procedure for validation

Prepare samples by adding 0,25ml, 0,5ml, 1ml, 1,5ml and 2ml of stock solution P to 1l of deionized water. In addition 50µl of stock solution Istd1 of benzylbutyl phthalate in acetone (c=10mg/ml) are added as internal standard.

Add 1ml acetone to each prepared 1l water sample and mix thoroughly to ensure homogenisation.

Take 5 portions of 100ml from each 1l water sample and proceed as described above. Compare results with validation requirements.

Annex C Peer Review Reports

Annex C1 Peer review report AIJU

Peer Review: "Methods Development for the Determination of Plasticisers in Toys". RESULTS FROM PEER REVIEW LABORATORY: AIJU.

1. Scope

In reported document CEN/TC 52/WG 9/TG 2 N151 it was proposed a method for the analysis of plasticisers in aqueous solution (obtained by extraction of toy samples with water) by the lead laboratory. The plasticisers to be analysed as well as the target concentrations (limit values) are listed in table 1. The scope of the peer review action reported in this paper is to revalidate this method.

Table 1: Preservatives.

Substance	**CAS Number**	**in 100ml H_2O**
Tributyl citrate	77-94-1	170µg
Tributyl *O*-acetyl citrate	77-90-7	170µg
Triethyl citrate	77-93-0	170µg
Triethyl *O*-acetylcitrate	77-89-4	170µg
Bis(2-ethylhexyl) adipate	103-23-1	100µg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	170µg
Bis(2-butoxyethyl) adipate	141-18-4	170µg
Dioctyl adipate	123-79-5	170µg
Diisodecyl adipate	27178-16-1	170µg
Bis(2-ethylhexyl) azelate	103-24-2	170µg
Bis(2-ethylhexyl) sebacate	122-62-3	170µg
Butyl benzoate	136-60-7	1700µg as benzoic acid
Di(ethylene glycol) dibenzoate	120-55-8	1700µg
Di(propylene glycol) dibenzoate	94-51-9	1700µg
Tributyl phosphate	126-73-8	170µg
Triphenyl phosphate	115-86-6	ND (~1µg)*
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	ND (~1µg)*
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	ND (~1µg)*
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	ND (~1µg)*
Bis(2-ethylhexyl) phthalate	117-81-7	12µg
Diisononyl phthalate	68515-48-0	50µg

* ND=Not detectable, to be determined by lead laboratory, estimated to be about 1µg

2. Principle

An aqueous solution of plasticisers is subjected to a single liquid/liquid extraction using toluene:ethylacetate 95:5 in a separatory funnel. The concentrations are determined by GC/MS in SIM-mode using a non-polar column. For quantification both external and internal standards are used.

3. Chemicals

3.1. Solvents

Acetone, GC grade

Toluene, GC grade

Ethylacetate, GC grade

Solvent Mixture: Mixture containing 95% toluene/5% ethylacetate (v/v)

Water deionized, Milli-Q quality

3.2. Plasticisers

The following plasticisers supplied by the lead lab were used in this work.

Tributyl citrate	Butyl benzoate
Tributyl *O*-acetyl citrate	Di(ethylene glycol) dibenzoate
Triethyl citrate	Di(propylene glycol) dibenzoate
Triethyl *O*-acetylcitrate	Tributyl phosphate
Bis(2-ethylhexyl) adipate	Triphenyl phosphate
Bis[2-(2-butoxyethoxy)ethyl] adipate	Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate
Bis(2-butoxyethyl) adipate	Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate
Dioctyl adipate	Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate
Diisodecyl adipate	Bis(2-ethylhexyl) phthalate
Bis(2-ethylhexyl) azelate	Diisononyl phthalate
Bis(2-ethylhexyl) sebacate	Benzylbutyl phthalate (internal standard)

4. Apparatus

4.1. Gas-chromatograph-mass spectrometry:

Perkin-Elmer AutoSystem XL GC, TurboMass Gold Mass Spectrometer.

Column: Phenomenex Zebron ZB-5, 30 m x 0.25mm (ID) x 0.25 um (film thickness).

Carrier gas: Helium.

Injector temperature: 275 ºC.

Injection Volume: 1 ul.

Injection type: split.

Column flow: 1.0 ml/min.

Split flow: 10 ml/min.

Solvent delay: 5 min.

Ionisation Potential: 70 eV.

Source temperature: 150 ºC.

Inlet Line temperature: 290 ºC.

Run time: 40 min.

Acquisition mode: SIR.

Oven program:

Initial Temperature (ºC)	Hold time (min)	Rate (ºC/min)	Final temperature (ºC	Final hold time (min)
100	1	7	300	10

Quantitation: List of target and qualifier ions for plasticisers:

Substance	**Target Ion**	**Qualifier**
Tributyl citrate	129	185
Tributyl *O*-acetyl citrate	185	129
Triethyl citrate	157	115
Triethyl *O*-acetylcitrate	157	203
Bis(2-ethylhexyl) adipate	129	111
Bis[2-(2-butoxyethoxy)ethyl] adipate	99	85
Bis(2-butoxyethyl) adipate	85	111
Dioctyl adipate	129	241
Diisodecyl adipate	129	111
Bis(2-ethylhexyl) azelate	171	112
Bis(2-ethylhexyl) sebacate	185	112
Butyl benzoate	105	123
Di(ethylene glycol) dibenzoate	105	149
Di(propylene glycol) dibenzoate	105	163
Tributyl phosphate	99	155
Triphenyl phosphate	325	169
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	165	179
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	368	165
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	368	165
Bis(2-ethylhexyl) phthalate	149	167
Diisononyl phthalate	149	293
Benzylbutyl phthalate (internal standard)	149	206

Due to interferences four runs using different time windows were required:

Run A

Time (min)	Monitored ions
7-17	99, 105, 115, 123, 155, 157, 203
19-23.95	85, 111, 129, 149, 185
24-26	105, 129, 149, 241
26.5-40	85, 99, 112, 171

Run B

Time (min)	Monitored ions
22-23.56	149, 206
23.58-25.5	149, 167, 325, 169, 105, 163
25.6-40	165, 179, 368, 185, 112

Run C

Time (min)	Monitored ions
26-40	129, 111

Run D

Time (min)	Monitored ions
26-40	149, 293

4.2. Basic Laboratoty Apparatus

Separatory funnels 250 ml

Measuring cylinders, glass

Ultrasonic bath - frequency 47 kHz

Pipettes with an accuracy of ± 0.5 µl or better

Analytic balance, capable of measuring 0.1 mg at least

Usual laboratory glass ware

5. Procedure

5.1. General

All glass ware and other items in contact with the sample or standard solutions were rinsed twice with acetone.

5.2. Stock solutions

A stock solution in acetone was prepared containing benzylbutyl phthalate to the nearest of 10 mg/ml (Stock solution Istd1). A dilution 1:10 in acetone was prepared to obtain a concentration of 1 mg/ml (Stock solution Istd2).

A stock solution in acetone was prepared containing all plasticisers of the following concentration levels (Stock solution P):

Table 2: Plasticisers stock solution P.

Substance	**Concentration (mg/ml)**
Tributyl citrate	1,70
Tributyl *O*-acetyl citrate	1,73
Triethyl citrate	1,68
Triethyl *O*-acetylcitrate	1,70
Bis(2-ethylhexyl) adipate	1,03
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,69
Bis(2-butoxyethyl) adipate	1,72
Dioctyl adipate	1,78
Diisodecyl adipate	1,70
Bis(2-ethylhexyl) azelate	1,70
Bis(2-ethylhexyl) sebacate	1,72
Butyl benzoate (*)	17,29
Di(ethylene glycol) dibenzoate	17,13
Di(propylene glycol) dibenzoate	17,02
Tributyl phosphate	1,70
Triphenyl phosphate	0,14
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0,22
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	0,11
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	0,12
Bis(2-ethylhexyl) phthalate	0,14
Diisononyl phthalate	0,51

(*) The concentration of butyl benzoate was chosen to obtain a level of 17 mg/ml as benzoic acid.

5.3. Calibration standards

Stock solution P was diluted to obtain calibration standards at a 200%, 150%, 100%, 50% and 25% level. Toluene was use as a solvent.

Calibration standard solutions were prepared, as follows:

200%: 2 ml of stock standard solution P to a 100 ml volumetric flask with toluene

150%: 1.5 ml of stock standard solution P to a 100 ml volumetric flask with toluene
100%: 1 ml of stock standard solution P to a 100 ml volumetric flask with toluene
50%: 0.5 ml of stock standard solution P to a 100 ml volumetric flask with toluene
25%: 0.25 ml of stock standard solution P to a 100 ml volumetric flask with toluene

Stock solution Istd1 (benzylbutyl phthalate in acetone, c=10 mg/ml) was added as internal standard to obtain a concentration of 5 μg/ml. This was achieved, by adding 50 μl of the stock solution Istd1 to the 100 ml diluted stock solutions.
In the following table, calibration range is shown.

Table 3: Plasticisers calibration range.

	Concentration (μg/ml)				
Substance	**25%**	**50%**	**100%**	**150%**	**200%**
Tributyl citrate	4,25	8,51	17,02	25,52	34,03
Tributyl *O*-acetyl citrate	4,32	8,63	17,26	25,90	34,53
Triethyl citrate	4,19	8,38	16,75	25,13	33,51
Triethyl *O*-acetylcitrate	4,24	8,48	16,97	25,46	33,94
Bis(2-ethylhexyl) adipate	2,59	5,17	10,35	15,52	20,69
Bis[2-(2-butoxyethoxy)ethyl] adipate	4,23	8,46	16,93	25,39	33,85
Bis(2-butoxyethyl) adipate	4,29	8,58	17,16	25,74	34,32
Dioctyl adipate	4,45	8,90	17,81	26,71	35,62
Diisodecyl adipate	4,24	8,48	16,97	25,45	33,93
Bis(2-ethylhexyl) azelate	4,24	8,48	16,97	25,46	33,94
Bis(2-ethylhexyl) sebacate	4,29	8,58	17,16	25,74	34,32
Butyl benzoate (*)	43,23	86,46	172,92	259,38	345,84
Di(ethylene glycol) dibenzoate	42,82	85,64	171,29	256,93	342,58
Di(propylene glycol) dibenzoate	42,54	85,09	170,18	255,26	340,35
Tributyl phosphate	4,26	8,53	17,06	25,58	34,11
Triphenyl phosphate	0,34	0,68	1,36	2,04	2,73
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0,56	1,12	2,25	3,38	4,50
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	0,28	0,56	1,12	1,68	2,24
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	0,30	0,60	1,21	1,82	2,42
Bis(2-ethylhexyl) phthalate	0,34	0,68	1,35	2,03	2,71
Diisononyl phthalate	1,28	2,55	5,10	7,65	10,21
Benzylbutyl phthalate (internal standard)	5,06	5,06	5,06	5,06	5,06

5.4.Calibration Curves

Three replicates of calibration plasticisers standards were injected. In the following table, linear equations and correlation coefficients are shown. The internal standard has been used for establishing calibration curves.

Table 4: Linearity for Plasticisers.

Substance	**Linear equation**	**Correlation coefficient (r)**	**Retention time(min)**
Tributyl citrate	y = 0,0989x + 0,3112	0,9998	20.9
Tributyl *O*-acetyl citrate	y = 0,1735x + 0,1389	0,9963	21,8
Triethyl citrate	y = 0,2601x + 0,0726	0,9989	13.5
Triethyl *O*-acetylcitrate	y = 0,6875x - 0,7195	0,9995	14,9
Bis(2-ethylhexyl) adipate	y = 0,2314x + 0,5342	0,9997	23,4
Bis[2-(2-butoxyethoxy)ethyl] adipate	y = 0,0132x + 0,1612	0,9977	27,9
Bis(2-butoxyethyl) adipate	y = 0,1301x + 0,0118	0,9976	22,1
Dioctyl adipate	y = 0,4484x - 1,3384	0,9986	25,0
Diisodecyl adipate	y = 0,1021x - 0,1241	0,9991	26,9
Bis(2-ethylhexyl) azelate	y = 0,2213x - 0,1245	0,9961	26,8
Bis(2-ethylhexyl) sebacate	y = 0,1887x - 0,4292	0,9991	27,8
Butyl benzoate (*)	y = 0,2871x + 256,5	0,9975	8,8
Di(ethylene glycol) dibenzoate	y = 0,2733x - 0,5378	0,9981	24,4
Di(propylene glycol) dibenzoate	y = 1,5979x - 45,5	0,9986	24.5
Tributyl phosphate	y = 0,7574x - 0,6922	0,9999	13,3
Triphenyl phosphate	y = 0,0402x - 0,0081	0,9985	23,6
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	y = 0,1266x - 0,0427	0,9985	25,7
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	y = 0,0194x - 0,003	0,9993	26,4
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	y = 0,0195x - 0,032	0,9985	27,3
Bis(2-ethylhexyl) phthalate	y = 0,7418x - 0,3262	0,9992	25,2
Diisononyl phthalate	y = 0,2506x - 0,0209	0,9974	28.2

5.4.1.- Determination of LOD/LOQ.

The limit of detection (LOD) and limit of quantitation (LOQ) of the aqueous extraction method are shown in the next table for the plasticisers. Both LOD and LOQ were calculated based on signal/noise ratio.

Table 5: LOD and LOQ for Plasticisers.

Substance	**LOD (µg/100 ml H_2O)**	**LOQ (µg/100 ml H_2O)**
Tributyl citrate	0.8	2.4
Tributyl *O*-acetyl citrate	0.4	1.2
Triethyl citrate	0.4	1.2
Triethyl *O*-acetylcitrate	0.2	0.6
Bis(2-ethylhexyl) adipate	0.9	2.7
Bis[2-(2-butoxyethoxy)ethyl] adipate	1.1	3.3
Bis(2-butoxyethyl) adipate	0.8	2.4
Dioctyl adipate	0.3	0.9
Diisodecyl adipate	3.0	9.0
Bis(2-ethylhexyl) azelate	0.9	2.7
Bis(2-ethylhexyl) sebacate	1.2	3.6
Butyl benzoate (*)	0.1	0.3
Di(ethylene glycol) dibenzoate	0.3	0.9
Di(propylene glycol) dibenzoate	0.2	0.6
Tributyl phosphate	1.3	3.9
Triphenyl phosphate	0.3	0.9
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	0.6	1.8
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	1.2	3.6
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	1.5	4.5
Bis(2-ethylhexyl) phthalate	0.6	1.8
Diisononyl phthalate	0.8	2.4

5.5. Sample Extraction

A blank sample was prepared by adding 50 µl of stock solution Istd1 of benzylbutyl phthalate in acetone (c=10 mg/ml) to 1 l of deionized water.

A water sample was prepared by adding 50 µl of stock solution Istd2 of benzylbutyl phthalate in acetone (c=1 mg/ml) to 100 ml of deionized water.

100 ml of the blank or water sample was extracted with 10 ml of the solvent mixture containing 95% toluene/5% ethylacetate (v/v) by shaking in a 250 ml separatory funnel for 1 minute. 10-20 minutes were elapsed until the two phases were set apart and the upper layer was drawn off.

No plasticisers were detected in the blank or water sample solutions.

5.6. Validation

Samples were prepared by adding 0.25 ml, 0.5 ml, 1 ml, 1.5 ml and 2 ml of stock solution P to 1 l of deionized water. In addition, 50 µl of stock solution Istd1 of benzylbutyl phthalate in acetone (c=10 mg/ml) were added as internal standard.

After that, 1 ml acetone was added to each prepared 1 l water sample and mixed thoroughly to ensure homogenisation.

5 portions of 100 ml from each 1 l water sample were taken. For each portion, sample was extracted with 10 ml of the solvent mixture containing 95% toluene/5% ethylacetate (v/v) by shaking in a 250 ml separatory funnel for 1 minute. 10-20 minutes were elapsed until the two phases were set apart and the upper layer was drawn off. In some cases, a bad separation between both phases was observed even after 1 hour.

5.6.1. Precision

The relative standard deviation should be bellow the following limits:

21% for a concentration of 0.01 µg/g (=1 µg/100 ml H_2O)
15% for a concentration of 0.1 µg/g (=10 µg/100 ml H_2O)
11% for a concentration of 1 µg/g (=100 µg/100 ml H_2O)

The following tables show results obtained. All measured values are in compliance with these limits.

Table 6: Precision at 25% of limit.

Substance	**Mean (µg/100 ml H_2O)**	**RSD (%)**
Tributyl citrate	32.1	8.9
Tributyl *O*-acetyl citrate	34.3	1.3
Triethyl citrate	38.4	2.0
Triethyl *O*-acetylcitrate	38.9	2.5
Bis(2-ethylhexyl) adipate	18.6	5.1
Bis[2-(2-butoxyethoxy)ethyl] adipate	35.1	4.7
Bis(2-butoxyethyl) adipate	32.0	7.5
Dioctyl adipate	39.9	2.4
Diisodecyl adipate	35.0	6.1
Bis(2-ethylhexyl) azelate	32.3	2.1
Bis(2-ethylhexyl) sebacate	40.5	6.5
Butyl benzoate (*)	395.0	2.6
Di(ethylene glycol) dibenzoate	343.5	5.2
Di(propylene glycol) dibenzoate	422.5	3.9
Tributyl phosphate	39.3	3.2
Triphenyl phosphate	3.2	5.6
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	5.0	4.8
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	2.7	1.8
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	2.8	2.9
Bis(2-ethylhexyl) phthalate	3.0	9.4
Diisononyl phthalate	11.2	6.0

Table 7: Precision at 50% of limit.

Substance	**Mean (µg/100 ml H_2O)**	**RSD (%)**
Tributyl citrate	65.7	4.5
Tributyl *O*-acetyl citrate	88.1	3.9
Triethyl citrate	72.0	3.7
Triethyl *O*-acetylcitrate	69.4	9.0
Bis(2-ethylhexyl) adipate	37.2	3.5
Bis[2-(2-butoxyethoxy)ethyl] adipate	65.2	5.2
Bis(2-butoxyethyl) adipate	66.9	3.5
Dioctyl adipate	64.5	4.2
Diisodecyl adipate	60.2	3.6
Bis(2-ethylhexyl) azelate	65.9	2.7
Bis(2-ethylhexyl) sebacate	83.8	3.3
Butyl benzoate (*)	843.6	2.9
Di(ethylene glycol) dibenzoate	706.1	2.3
Di(propylene glycol) dibenzoate	706.2	3.2
Tributyl phosphate	76.0	2.8
Triphenyl phosphate	6.6	6.9
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	11.3	6.7
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	5.4	6.2
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	6.4	5.8
Bis(2-ethylhexyl) phthalate	6.9	5.2
Diisononyl phthalate	25.8	3.1

Table 8: Precision at 100% of limit.

Substance	**Mean (µg/100 ml H_2O)**	**RSD (%)**
Tributyl citrate	141.3	3.5
Tributyl *O*-acetyl citrate	148.8	4.4
Triethyl citrate	165.3	3.6
Triethyl *O*-acetylcitrate	170.1	7.1
Bis(2-ethylhexyl) adipate	79.9	6.9
Bis[2-(2-butoxyethoxy)ethyl] adipate	164.1	5.4
Bis(2-butoxyethyl) adipate	153.6	2.9
Dioctyl adipate	172.7	3.2
Diisodecyl adipate	168.0	2.7
Bis(2-ethylhexyl) azelate	144.3	3.6
Bis(2-ethylhexyl) sebacate	145.3	3.1
Butyl benzoate (*)	1572.8	5.8
Di(ethylene glycol) dibenzoate	1306.4	2.9
Di(propylene glycol) dibenzoate	1375.5	2.8
Tributyl phosphate	133.2	4.9
Triphenyl phosphate	12.6	3.7
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	18.0	4.2
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	10.1	5.3
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	12.0	6.6
Bis(2-ethylhexyl) phthalate	14.0	4.1
Diisononyl phthalate	50.3	3.5

Table 9: Precision at 150% of limit.

Substance	**Mean (µg/100 ml H_2O)**	**RSD (%)**
Tributyl citrate	237.9	0.4
Tributyl *O*-acetyl citrate	231.3	5.8
Triethyl citrate	207.5	4.9
Triethyl *O*-acetylcitrate	249.3	1.7
Bis(2-ethylhexyl) adipate	136.7	2.1
Bis[2-(2-butoxyethoxy)ethyl] adipate	250.8	4.3
Bis(2-butoxyethyl) adipate	256.5	7.6
Dioctyl adipate	257.2	1.5
Diisodecyl adipate	237.8	1.9
Bis(2-ethylhexyl) azelate	208.6	2.8
Bis(2-ethylhexyl) sebacate	253.4	2.2
Butyl benzoate (*)	2596.6	4.2
Di(ethylene glycol) dibenzoate	2084.5	1.8
Di(propylene glycol) dibenzoate	2353.0	1.5
Tributyl phosphate	246.3	2.2
Triphenyl phosphate	20.3	4.7
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	30.8	6.1
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	16.5	2.5
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	17.1	4.3
Bis(2-ethylhexyl) phthalate	18.8	5.4
Diisononyl phthalate	77.6	1.7

Table 10: Precision at 200% of limit.

Substance	**Mean (μg/100 ml H_2O)**	**RSD (%)**
Tributyl citrate	344.9	1.8
Tributyl *O*-acetyl citrate	351.2	1.7
Triethyl citrate	298.4	4.6
Triethyl *O*-acetylcitrate	336.0	3.1
Bis(2-ethylhexyl) adipate	199.4	5.3
Bis[2-(2-butoxyethoxy)ethyl] adipate	335.3	5.8
Bis(2-butoxyethyl) adipate	346.4	1.7
Dioctyl adipate	295.4	2.5
Diisodecyl adipate	293.2	2.3
Bis(2-ethylhexyl) azelate	318.5	3.8
Bis(2-ethylhexyl) sebacate	266.2	2.6
Butyl benzoate (*)	3397.0	1.7
Di(ethylene glycol) dibenzoate	3388.0	5.6
Di(propylene glycol) dibenzoate	3392.6	2.5
Tributyl phosphate	316.6	3.3
Triphenyl phosphate	26.9	2.1
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	39.5	2.6
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	22.6	5.8
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	24.0	3.6
Bis(2-ethylhexyl) phthalate	25.7	2.9
Diisononyl phthalate	107.1	2.5

5.6.2. Recovery

The recommended recovery targets for plasticisers are:

80-110% for a concentration levels 0.1 μg/g to 10 μg/g (=10 μg/100 ml H_2O to 1000 μg/100 ml H_2O)
60-115% for 0.01 μg/g (=1 μg/100 ml H_2O)

The following table shows results obtained. Some values are lower the limit, but in general, all measured values are in compliance with these limits.

Table 11: Recovery for Plasticisers.

	Recovery (%)				
Substance	**25%**	**50%**	**100%**	**150%**	**200%**
Tributyl citrate	75.5	77.4	83.2	93.4	101.7
Tributyl *O*-acetyl citrate	79.6	102.3	86.4	89.5	102.0
Triethyl citrate	91.9	86.0	98.9	82.8	89.3
Triethyl *O*-acetylcitrate	91.8	82.0	100.4	98.2	99.3
Bis(2-ethylhexyl) adipate	72.1	71.9	77.4	88.3	96.6
Bis[2-(2-butoxyethoxy)ethyl] adipate	83.0	77.2	97.1	99.0	99.3
Bis(2-butoxyethyl) adipate	74.7	78.1	89.6	99.9	101.2
Dioctyl adipate	89.7	72.5	97.2	96.5	83.2
Diisodecyl adipate	82.6	71.0	99.2	93.7	86.7
Bis(2-ethylhexyl) azelate	76.2	77.8	85.2	82.1	94.1
Bis(2-ethylhexyl) sebacate	94.5	97.8	84.8	98.7	77.8
Butyl benzoate (*)	91.5	97.7	91.1	100.4	98.5
Di(ethylene glycol) dibenzoate	80.3	82.6	76.4	81.3	99.2
Di(propylene glycol) dibenzoate	99.4	83.1	81.0	92.4	100.0
Tributyl phosphate	92.2	89.2	78.3	96.5	93.1
Triphenyl phosphate	95.2	96.7	93.0	99.4	99.0
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	89.4	100.6	80.1	91.4	88.0
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	98.3	96.8	90.2	98.9	101.6
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	93.0	106.7	99.7	94.2	99.5
Bis(2-ethylhexyl) phthalate	88.2	102.2	103.9	92.7	95.1
Diisononyl phthalate	87.8	101.4	98.7	101.7	105.2

Annex C2 Peer review report LGA

Peer review report

DETERMINATION OF PLASTICIZERS

for

CEN TC WG9 TG2
Safety of toys – Organic chemical compounds – Methods of analysis

2003-01-23

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1. Introduction

This validation report is based on the peer review laboratory contract between LGC and LGA.
It is also based on the interim report (N151July 2002) and the validation report (N 181 October 2002) of the lead laboratory.

2. Substances requiring methods of analysis

Table 1: Plasticizers requiring methods of analysis.

Substance	CAS Number	Limit In 100ml water
Tributyl citrate	77-94-1	170μg
Tributyl o-acetylcitrate	77-90-7	170μg
Triethyl citrate	77-93-0	170μg
Triethyl o-acetylcitrate	77-89-4	170μg
Bis(2-ethylhexyl) adipate	103-23-1	170μg
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3	170μg
Bis(2-butoxyethyl) adipate	141-18-4	170μg
Dioctyl adipate	123-79-5	170μg
Diisodecyl adipate	27178-16-1	170μg
Bis(2-ethylhexyl) azelate	103-24-2	170μg
Bis(2-ethylhexyl) sebacate	122-62-3	170μg
Butyl benzoate	136-60-7	170μg as benzoic acid
Diethylene glycol dibenzoate	120-55-8	170μg
Dipropylene glycol dibenzoate	94-51-9	170μg
Tributyl phosphate	126-73-8	170μg
Triphenyl phosphate	115-86-6	ND(≈1μg)*
Tri-o-tolyl phosphate, tri-o-cresyl phosphate	78-30-8	ND(≈1μg)*
Tri-m-tolyl phosphate, tri-m-cresyl phosphate	563-04-2	ND(≈1μg)*
Tri-p-tolyl phosphate, tri-p-cresyl phosphate	78-32-0	ND(≈1μg)*
Bis(2-ethylhexyl)phthalate	117-81-7	12μg
Diisononyl phthalate	68515-48-0	50μg

*Nd = not detectable, to be determined by lead laboratory, estimated to be about 1μg

3. Method of analysis

3.1 Apparatus

Gaschromatograph: HP 5890 Series II

Mass selective detector: HP5970

Autoinjector: HP6890

Analytical column: Optima delta-3 (Macherey & Nagel), dimensions: 30mx0,25mmx0,25µm

Injection volume: 1µl slitless

Carrier gas:	Helium
Injection:	splitless
Injector temperature:	200°C
Detector temperature:	300°C

Inlet temperature: 275°C

Oven temperature program: Init. Temp.: 100°C
Init. Time: 1min
Rate: 7°C/min
Final temp.: 300°C
Final time: 10min

Transfer line temp.:290°C

For Identification and quantification the qualifier and target ions listed in the interim report of lead laboratory (N151) were used.

3.2 Chemicals

Ethylacetate, purity >99%, Merck
Acetone, for residue analysis, Fluka
Toluene, for residue analysis, Fluka

3.3 Analytes

The standard solutions were prepared from the plasticizers sent by the lead laboratory.

3.4 Calibration Standards

The stock solutions and calibration standards were prepared as described in annex B (SOP) of the interim report of the lead laboratory (N 151).

A stock solution in acetone was prepared containing all plasticizers in concentrations near the concentrations of the following table.

Substance	**Concentration mg/l**
Tributyl citrate	1,7
Tributyl o-acetylcitrate	1,7
Triethyl citrate	1,7
Triethyl o-acetylcitrate	1,7
Bis(2-ethylhexyl) adipate	1,7
Bis[2-(2-butoxyethoxy)ethyl] adipate	1,7
Bis(2-butoxyethyl) adipate	1,7
Dioctyl adipate	1,7
Diisodecyl adipate	1,7
Bis(2-ethylhexyl) azelate	1,7
Bis(2-ethylhexyl) sebacate	1,7
Butyl benzoate	2,5
Diethylene glycol dibenzoate	1,7
Dipropylene glycol dibenzoate	1,7
Tributyl phosphate	1,7
Triphenyl phosphate	0,01
Tri-o-tolyl phosphate	0,01
Tri-m-tolyl phosphate	0,01
Tri-p-tolyl phosphate	0,01
Bis(2-ethylhexyl)phthalate	0,12
Diisononyl phthalate	0,5

A stock solution in acetone of benzylbutyl phthalate as an internal standard of 10mg/l is prepared = stock solution Istd1.

This solution is diluted 1:10 with acetone = stock solution Istd2.

The stock solution of plasticizers was diluted with toluene to obtain calibration standards with 25%, 50%, 100%, 150% and 200% of the concentrations given below.

Calibration standard 100%:

Substance	**µg in 1ml toluene**
Tributyl citrate	17
Tributyl o-acetylcitrate	17
Triethyl citrate	17
Triethyl o-acetylcitrate	17
Bis(2-ethylhexyl) adipate	17
Bis[2-(2-butoxyethoxy)ethyl] adipate	17
Bis(2-butoxyethyl) adipate	17
Dioctyl adipate	17
Diisodecyl adipate	17
Bis(2-ethylhexyl) azelate	17
Bis(2-ethylhexyl) sebacate	17
Butyl benzoate	17 (as benzoic acid)
Diethylene glycol dibenzoate	17
Dipropylene glycol dibenzoate	17
Tributyl phosphate	17
Triphenyl phosphate	0,1
Tri-o-tolyl phosphate	0,1
Tri-m-tolyl phosphate	0,1
Tri-p-tolyl phosphate	0,1
Bis(2-ethylhexyl)phthalate	1,2
Diisononyl phthalate	5

To this calibration standards stock solution Istd1 is added (50µl/100ml diluted stock solution). The internal standard concentration is 5µg/ml.

Aqueous samples were prepared by adding 0,25ml, 0,5ml, 1ml, 1,5ml and 2ml of stock solution to 1l of deionized water. 50µl of Istd1 in acetone were added as an internal standard.

3.5 Sample extraction

A blank is prepared by adding 50µl of Istd1 to 1l of deionized water.

100 ml of the blank or of the aqueous samples are extracted with 10ml of a solvent mixture containing 95%-vol toluene and 5%-vol ethylacetate by shaking in a 250ml separatory funnel for 1 minute. After separation of the two phases the upper layer is drawn up and used for analysis.

3.6 Analytical determination

Each calibration standard, blank and sample is analysed according to clause 3.1.

Calibration curves are established and used to determine the content of plasticizers in the samples.

4. Results of validation

4.1 Determination of LOD and LOQ, based on signal/noise ratio

Substance	**LOD** μg/100ml H_2O	**LOQ** μg/100ml H_2O
Tributyl citrate	1,71	5,12
Tributyl o-acetylcitrate	0,21	0,63
Triethyl citrate	1,15	3,45
Triethyl o-acetylcitrate	0,14	0,42
Bis(2-ethylhexyl) adipate	0,04	0,12
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,29	0,87
Bis(2-butoxyethyl) adipate	0,09	0,27
Dioctyl adipate	0,11	0,33
Diisodecyl adipate	3,02	9,06
Bis(2-ethylhexyl) azelate	0,17	0,51
Bis(2-ethylhexyl) sebacate	0,15	0,45
Butyl benzoate	0,05	0,15
Diethylene glycol dibenzoate	0,03	0,09
Dipropylene glycol dibenzoate	0,13	0,39
Tributyl phosphate	0,04	0,12
Triphenyl phosphate	0,16	0,48
Tri-o-tolyl phosphate	0,51	1,53
Tri-m-tolyl phosphate	0,16	0,48
Tri-p-tolyl phosphate	0,12	0,36
Bis(2-ethylhexyl)phthalate	0,04	0,12
Diisononyl phthalate	1,90	5,70

4.2 Precision

Precision at 25% of limit

Substance	Average Concentration µg/100ml H_2O	Standard deviation µg/100ml H_2O	RSD %
Tributyl citrate	39,81	1,40	3,51
Tributyl o-acetylcitrate	39,26	0,41	1,05
Triethyl citrate	42,76	2,20	5,15
Triethyl o-acetylcitrate	43,24	1,06	2,45
Bis(2-ethylhexyl) adipate	40,25	3,08	7,65
Bis[2-(2-butoxyethoxy)ethyl] adipate	41,01	1,73	4,22
Bis(2-butoxyethyl) adipate	44,74	2,02	4,53
Dioctyl adipate	38,75	2,00	5,15
Diisodecyl adipate	45,73	1,92	4,20
Bis(2-ethylhexyl) azelate	34,73	1,41	4,15
Bis(2-ethylhexyl) sebacate	34,28	1,34	3,91
Butyl benzoate	44,74	1,39	3,10
Diethylene glycol dibenzoate	41,2	0,94	2,29
Dipropylene glycol dibenzoate	46,5	2,17	4,66
Tributyl phosphate	46,02	1,59	3,46
Bis(2-ethylhexyl)phthalate	3,07	0,62	2,02
Diisononyl phthalate	14,02	0,15	1,07

Precision at 1 x LOQ

Substance	Average Concentration µg/100ml H_2O	Standard deviation µg/100ml H_2O	RSD %
Triphenyl phosphate	0,96	0,05	4,91
Tri-o-tolyl phosphate	1,21	0,06	5,36
Tri-m-tolyl phosphate	0,94	0,03	3,43
Tri-p-tolyl phosphate	1,15	0,07	6,45

Precision at 50% of limit

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Tributyl citrate	79,49	2,19	2,75
Tributyl o-acetylcitrate	78,48	2,53	3,22
Triethyl citrate	85,48	3,24	3,79
Triethyl o-acetylcitrate	86,52	2,68	3,10
Bis(2-ethylhexyl) adipate	80,48	3,36	4,12
Bis[2-(2-butoxyethoxy)ethyl] adipate	81,98	3,82	4,66
Bis(2-butoxyethyl) adipate	89,48	2,02	2,26
Dioctyl adipate	77,48	2,44	3,15
Diisodecyl adipate	91,52	4,44	4,85
Bis(2-ethylhexyl) azelate	69,47	1,56	2,24
Bis(2-ethylhexyl) sebacate	68,52	1,84	2,69
Butyl benzoate	89,52	3,69	4,12
Diethylene glycol dibenzoate	82,4	2,60	3,15
Dipropylene glycol dibenzoate	93,03	4,51	4,85
Tributyl phosphate	92,02	4,52	4,91
Bis(2-ethylhexyl)phthalate	6,17	0,26	4,25
Diisononyl phthalate	28,01	1,59	5,69

Precision at 2 x LOQ

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Triphenyl phosphate	1,93	0,09	4,80
Tri-o-tolyl phosphate	2,25	0,13	5,67
Tri-m-tolyl phosphate	1,85	0,10	5,21
Tri-p-tolyl phosphate	2,29	0,11	5,02

Precision at 100% of limit

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Tributyl citrate	159,02	7,33	4,61
Tributyl o-acetylcitrate	157,01	6,19	3,94
Triethyl citrate	170,98	6,67	3,90
Triethyl o-acetylcitrate	171,98	7,14	4,15
Bis(2-ethylhexyl) adipate	161,03	4,28	2,66
Bis[2-(2-butoxyethoxy)ethyl] adipate	164,05	4,00	2,44
Bis(2-butoxyethyl) adipate	178,95	9,13	5,10
Dioctyl adipate	155,02	4,17	2,69
Diisodecyl adipate	183,06	4,65	2,54
Bis(2-ethylhexyl) azelate	138,96	2,99	2,15
Bis(2-ethylhexyl) sebacate	137,03	5,29	3,86
Butyl benzoate	179,05	4,37	2,44
Diethylene glycol dibenzoate	165,01	4,42	2,68
Dipropylene glycol dibenzoate	186,04	5,67	3,05
Tributyl phosphate	184,30	4,85	2,63
Bis(2-ethylhexyl)phthalate	12,42	0,74	5,96
Diisononyl phthalate	56,03	1,36	2,43

Precision at 4 x LOQ

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Triphenyl phosphate	3,78	0,21	5,60
Tri-o-tolyl phosphate	4,49	0,22	4,91
Tri-m-tolyl phosphate	3,73	0,14	3,85
Tri-p-tolyl phosphate	4,59	0,17	3,69

Precision at 150% of limit

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Tributyl citrate	237,95	4,88	2,05
Tributyl o-acetylcitrate	235,59	9,1	3,86
Triethyl citrate	256,59	7,3	2,85
Triethyl o-acetylcitrate	259,02	6,37	2,46
Bis(2-ethylhexyl) adipate	268,47	13,48	5,02
Bis[2-(2-butoxyethoxy)ethyl] adipate	245,94	15,44	6,28
Bis(2-butoxyethyl) adipate	241,52	8,50	3,52
Dioctyl adipate	232,53	8,58	3,69
Diisodecyl adipate	274,47	9,63	3,51
Bis(2-ethylhexyl) azelate	208,54	8,36	4,01
Bis(2-ethylhexyl) sebacate	205,51	6,21	3,02
Butyl benzoate	268,59	15,66	5,83
Diethylene glycol dibenzoate	248,01	12,87	5,19
Dipropylene glycol dibenzoate	279,06	8,79	3,15
Tributyl phosphate	276,02	8,86	3,21
Bis(2-ethylhexyl)phthalate	18,51	0,90	4,89
Diisononyl phthalate	83,97	2,73	3,26

Precision at 6x LOQ

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Triphenyl phosphate	5,66	0,17	3,02
Tri-o-tolyl phosphate	6,72	0,22	3,31
Tri-m-tolyl phosphate	5,59	0,19	3,29
Tri-p-tolyl phosphate	9,91	0,30	3,01

Precision at 200% of limit

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Tributyl citrate	318,02	14,34	4,51
Tributyl o-acetylcitrate	313,95	6,44	2,05
Triethyl citrate	342,05	14,20	4,15
Triethyl o-acetylcitrate	346,03	8,48	2,45
Bis(2-ethylhexyl) adipate	318,05	18,00	5,65
Bis[2-(2-butoxyethoxy)ethyl] adipate	328,99	10,59	3,22
Bis(2-butoxyethyl) adipate	358,03	12,64	3,53
Dioctyl adipate	309,98	12,86	4,15
Diisodecyl adipate	366,01	15,37	4,20
Bis(2-ethylhexyl) azelate	274,05	11,37	4,15
Bis(2-ethylhexyl) sebacate	273,98	10,71	3,91
Butyl benzoate	358,05	11,10	3,10
Diethylene glycol dibenzoate	331,02	15,42	2,29
Dipropylene glycol dibenzoate	372,03	17,34	4,66
Tributyl phosphate	368,05	9,05	2,46
Bis(2-ethylhexyl)phthalate	24,71	0,50	2,02
Diisononyl phthalate	111,98	1,76	1,57

Precision at 8 x LOQ

Substance	**Average Concentration µg/100ml H_2O**	**Standard deviation µg/100ml H_2O**	**RSD %**
Triphenyl phosphate	7,61	0,19	2,51
Tri-o-tolyl phosphate	8,97	0,27	2,99
Tri-m-tolyl phosphate	7,46	0,18	2,43
Tri-p-tolyl phosphate	9,19	0,32	3,45

All results are in compliance with the limits given in CEN TC 52 WG9 TG2 N68rev4.

4.3 Recovery

Substance	25% of limit	50% of limit	100% of limit	150% of limit	200% of limit
Tributyl citrate	81	82	85	84	85
Tributyl o-acetylcitrate	92	91	95	99	98
Triethyl citrate	80	83	81	84	83
Triethyl o-acetylcitrate	91	95	92	96	97
Bis(2-ethylhexyl) adipate	95	89	92	98	99
Bis[2-(2-butoxyethoxy)ethyl] adipate	86	91	96	89	102
Bis(2-butoxyethyl) adipate	89	88	98	97	95
Dioctyl adipate	95	90	102	105	98
Diisodecyl adipate	95	91	96	103	99
Bis(2-ethylhexyl) azelate	98	90	99	88	102
Bis(2-ethylhexyl) sebacate	95	97	101	99	100
Butyl benzoate	87	88	95	98	97
Diethylene glycol dibenzoate	91	89	104	101	98
Dipropylene glycol dibenzoate	89	90	95	94	93
Tributyl phosphate	92	89	93	95	88
Bis(2-ethylhexyl)phthalate	99	98	88	101	104
Diisononyl phthalate	90	88	93	99	95

Substance	1xLOQ %	2xLOQ %	3xLOQ %	6xLOQ %	8xLOQ %
Triphenyl phosphate	88	83	89	87	93
Tri-o-tolyl phosphate	101	89	86	91	99
Tri-m-tolyl phosphate	82	81	85	89	86
Tri-p-tolyl phosphate	85	89	90	91	86

All results are in compliance with the limits given in CEN TC 52 WG9 TG2 N68rev4.

4.5 Linearity

Regression line 25% - 200% of limit

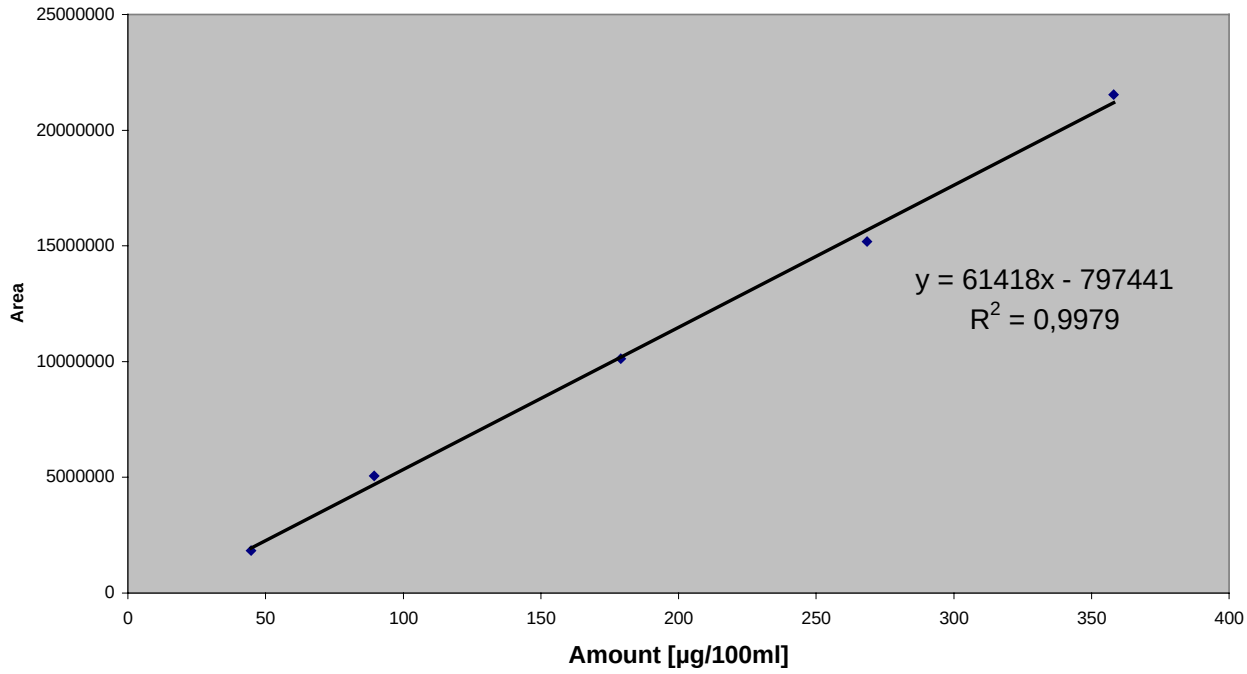
8.1.1.1 Substance	Corr. Coefficient (R)
Tributyl citrate	0,9972
Tributyl o-acetylcitrate	0,9953
Triethyl citrate	0,9960
Triethyl o-acetylcitrate	0,9981
Bis(2-ethylhexyl) adipate	0,9956
Bis[2-(2-butoxyethoxy)ethyl] adipate	0,9975
Bis(2-butoxyethyl) adipate	0,9980
Dioctyl adipate	0,9977
Diisodecyl adipate	0,9986
Bis(2-ethylhexyl) azelate	0,9955
Bis(2-ethylhexyl) sebacate	0,9965
Butyl benzoate	0,9979
Diethylene glycol dibenzoate	0,9960
Dipropylene glycol dibenzoate	0,9958
Tributyl phosphate	0,9956
Bis(2-ethylhexyl)phthalate	0,9985
Diisononyl phthalate	0,9958

Regression line 1x – 8x LOQ

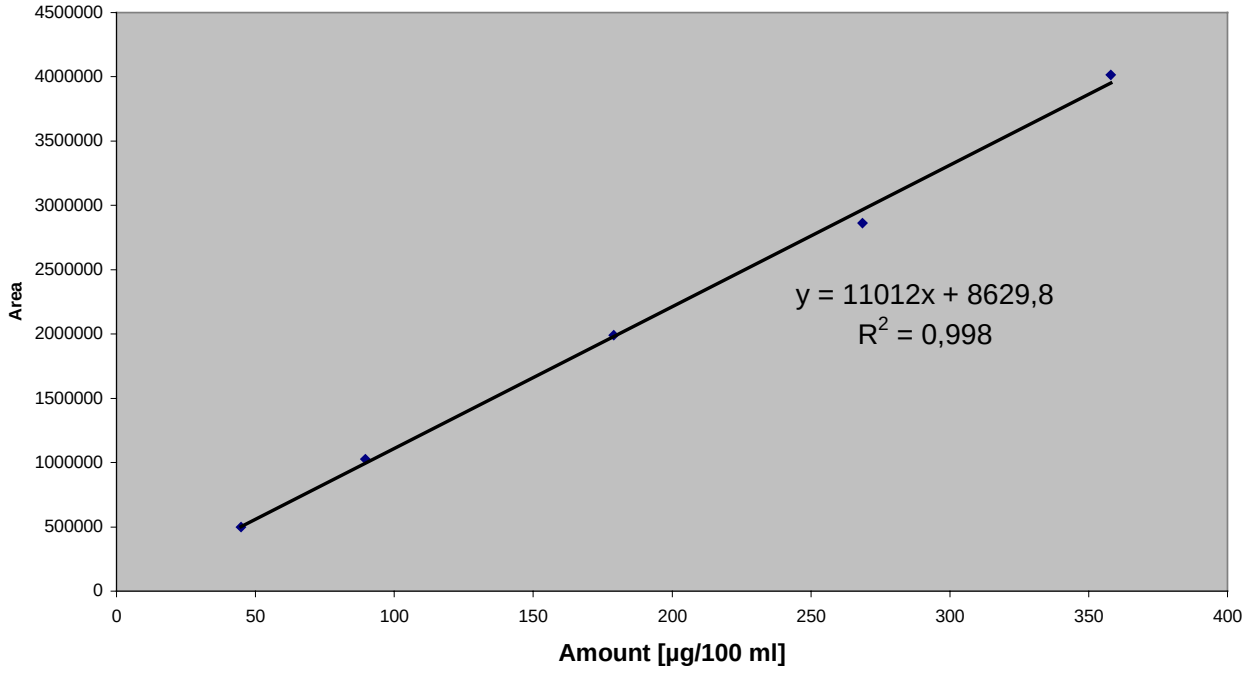
8.1.1.2 Substance	Corr. Coefficient (R)
Triphenyl phosphate	0,9976
Tri-o-tolyl phosphate	0,9974
Tri-m-tolyl phosphate	0,9975
Tri-p-tolyl phosphate	0,9961

The correlation coefficient is better than 0,995 for all plasticizers.

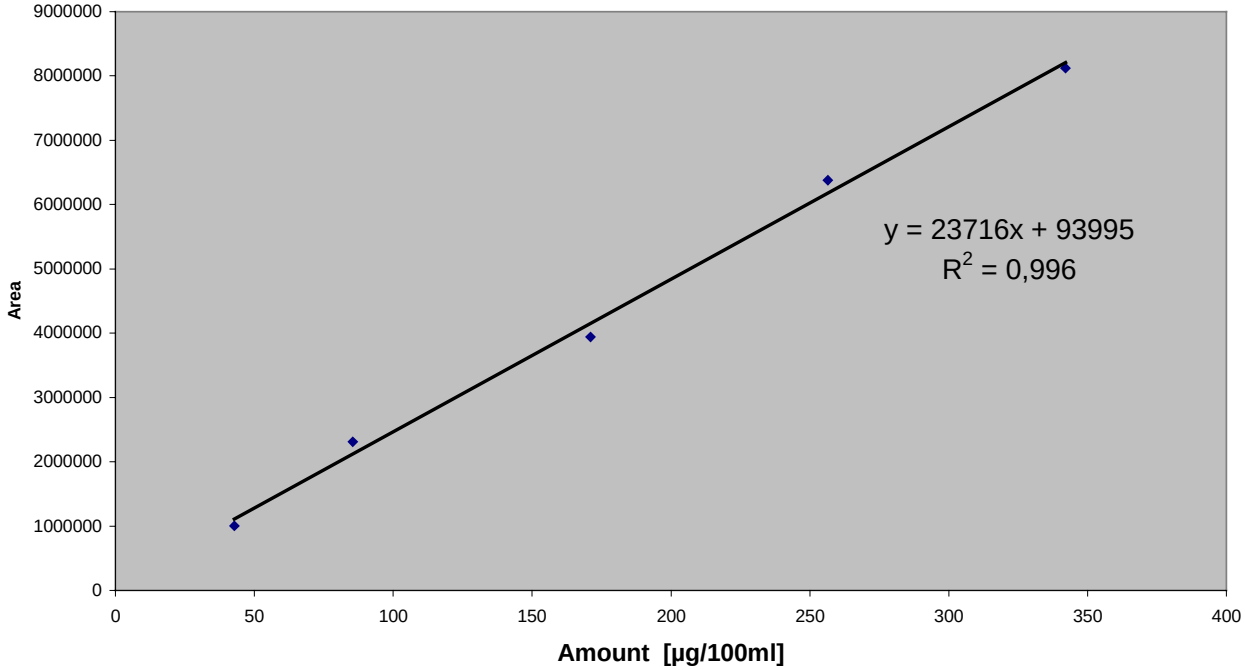
Butylbenzoate



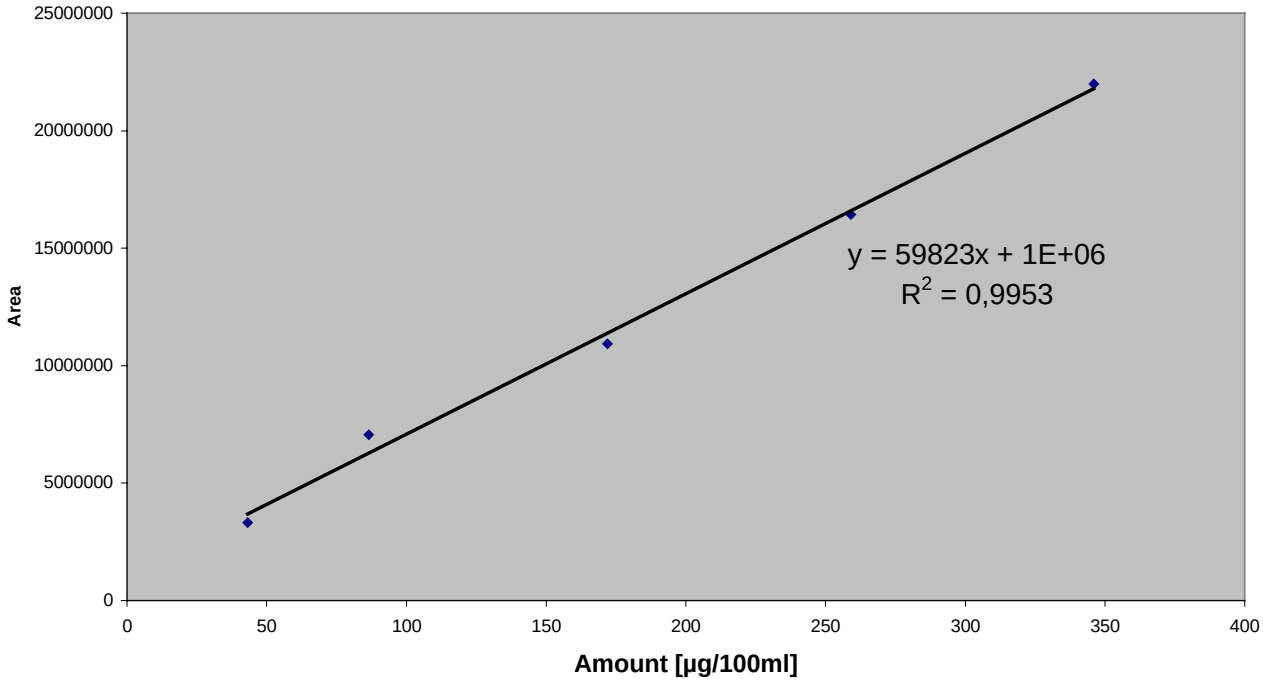
Bis (2-butoxyethyl) adipate



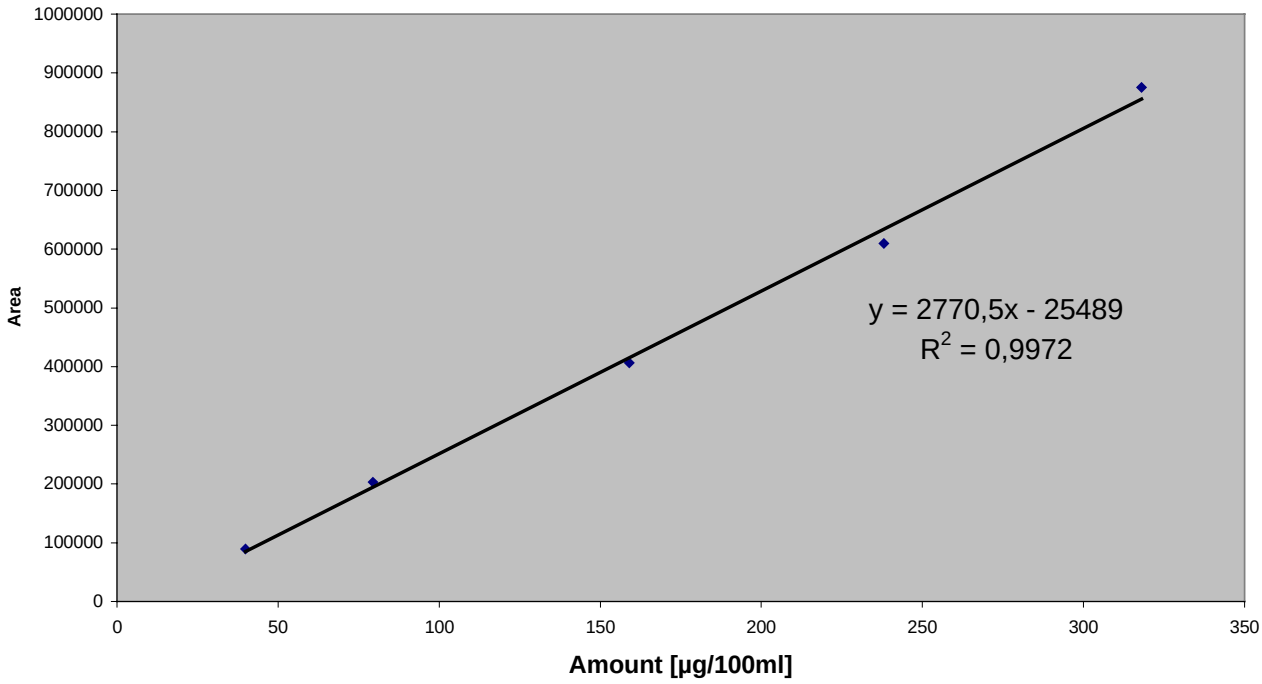
Triethyl citrate



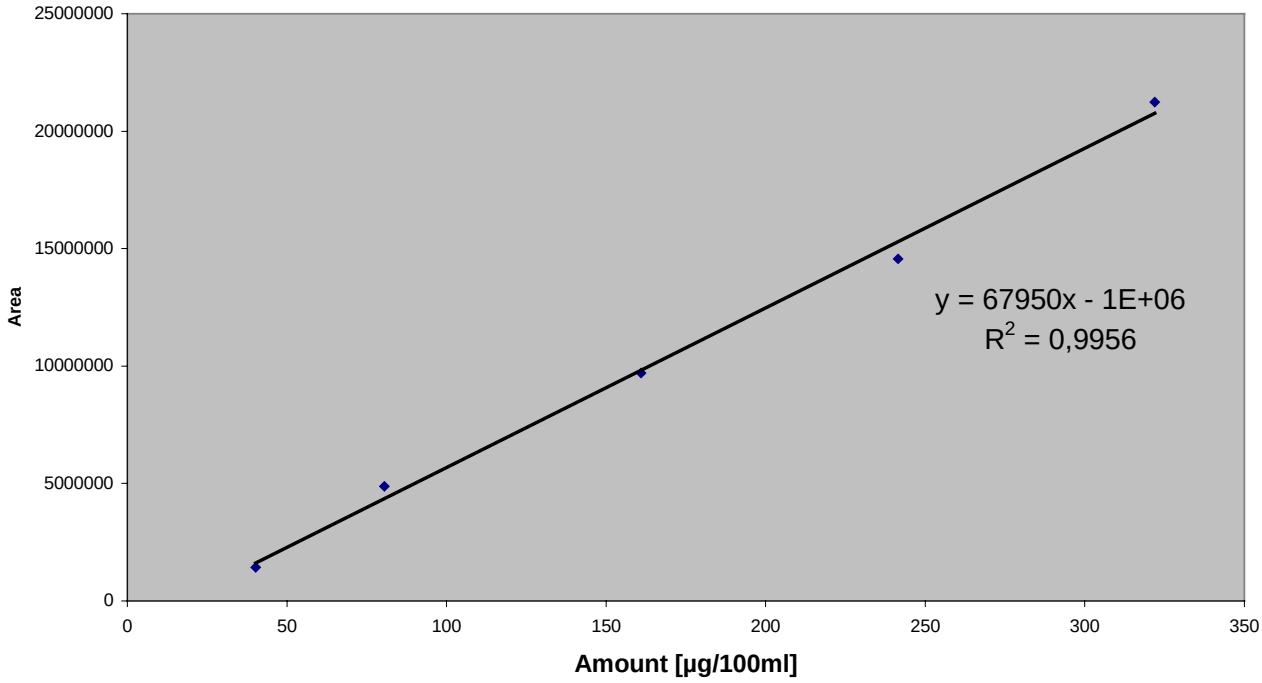
Triethyl o-acetyl citrate



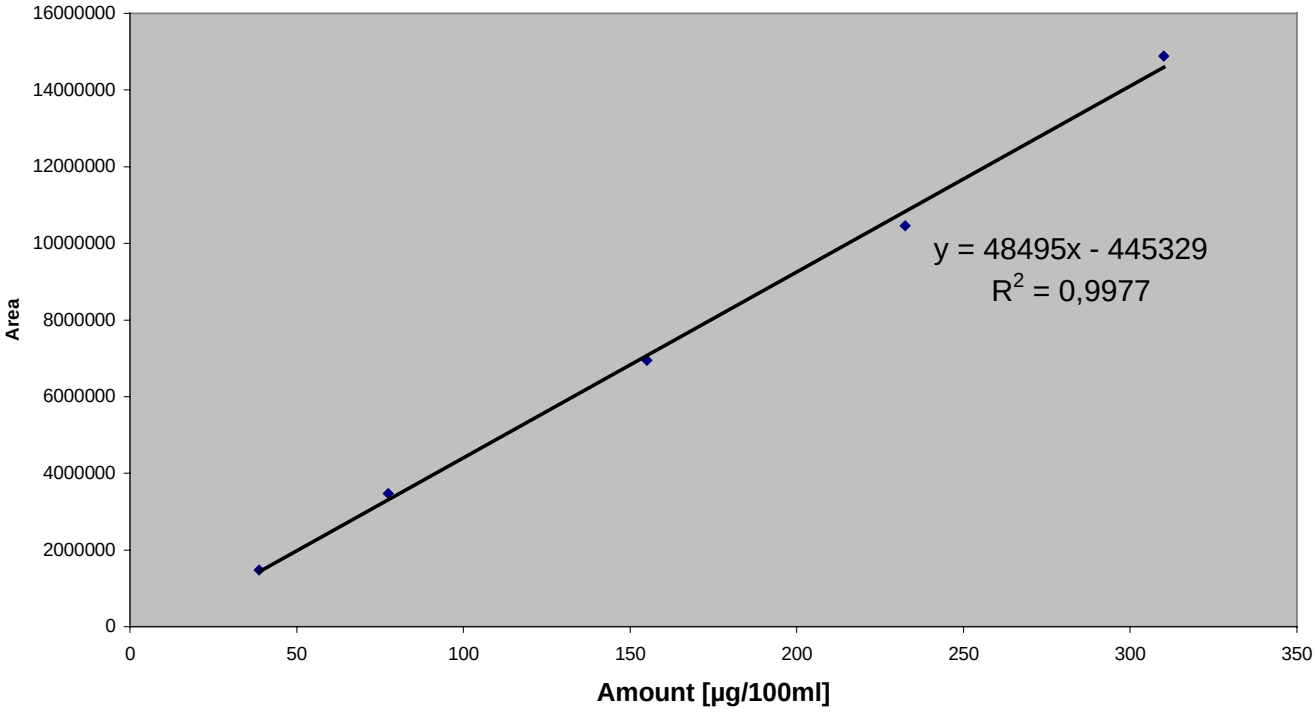
Tributyl citrate



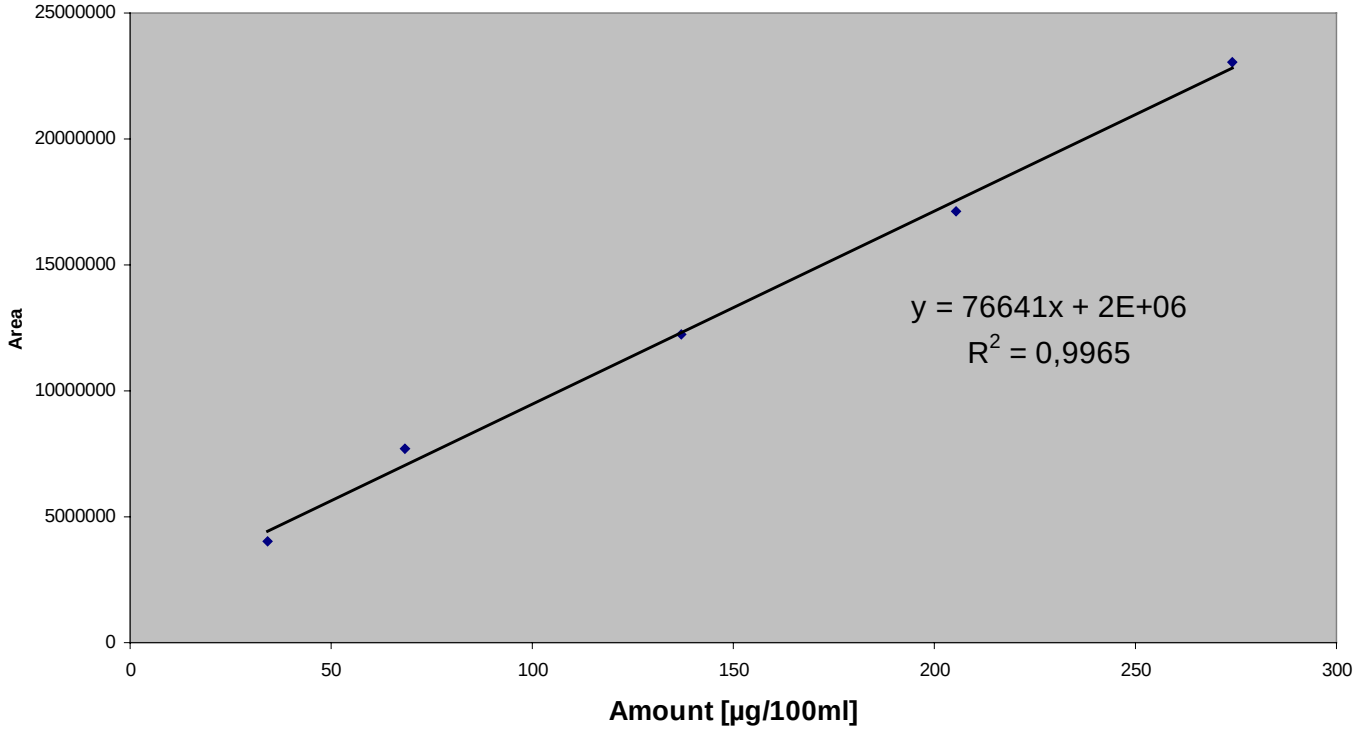
Bis (2-ethylhexyl) adipate



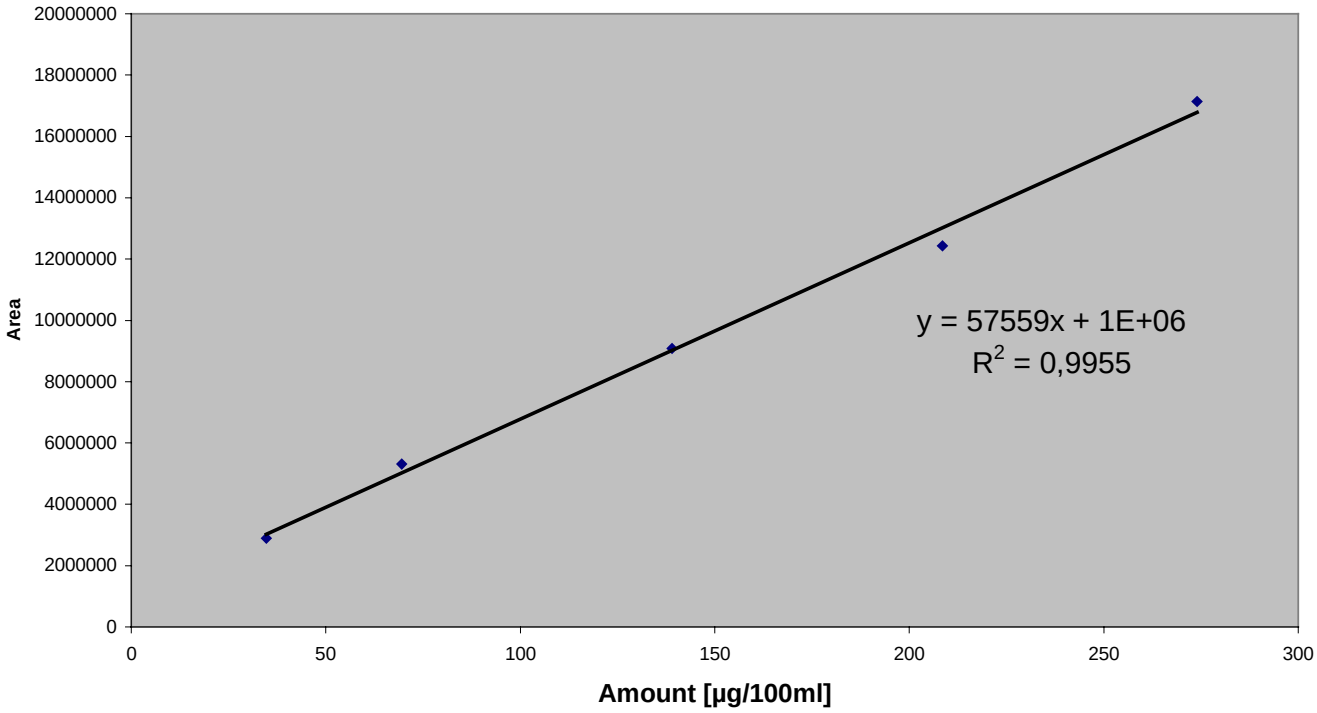
Dioctyl adipate



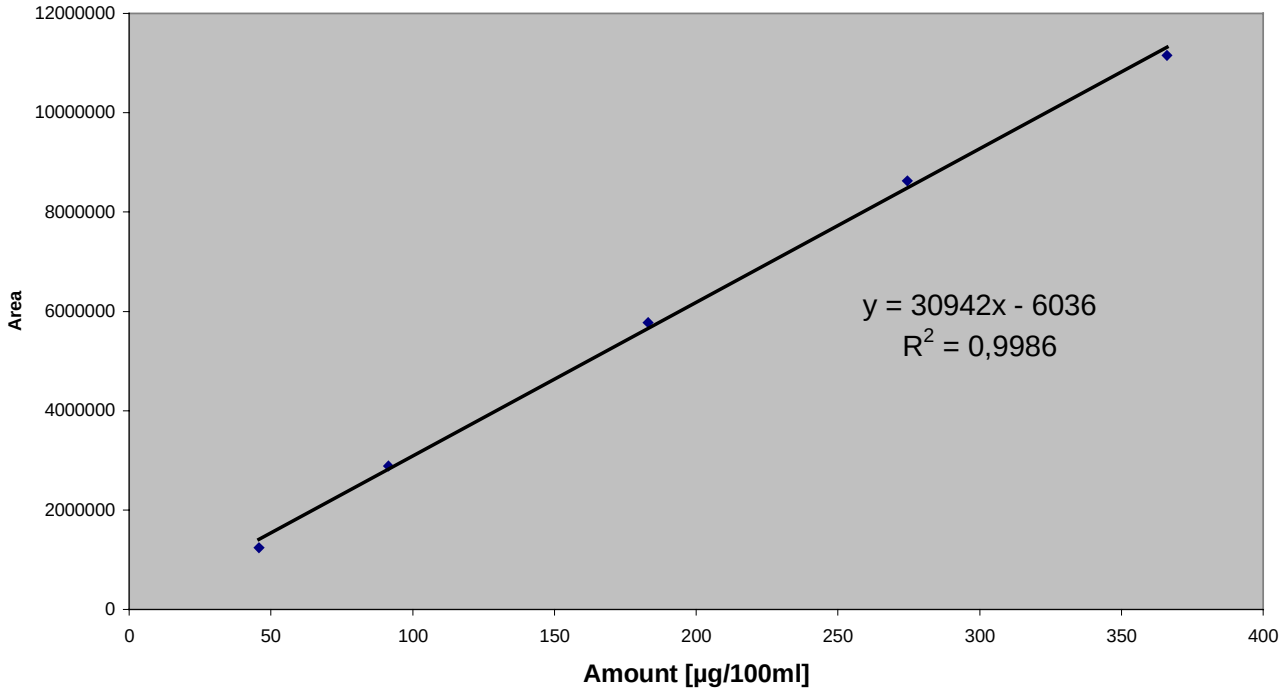
Bis (2-ethylhexyl) sebacate



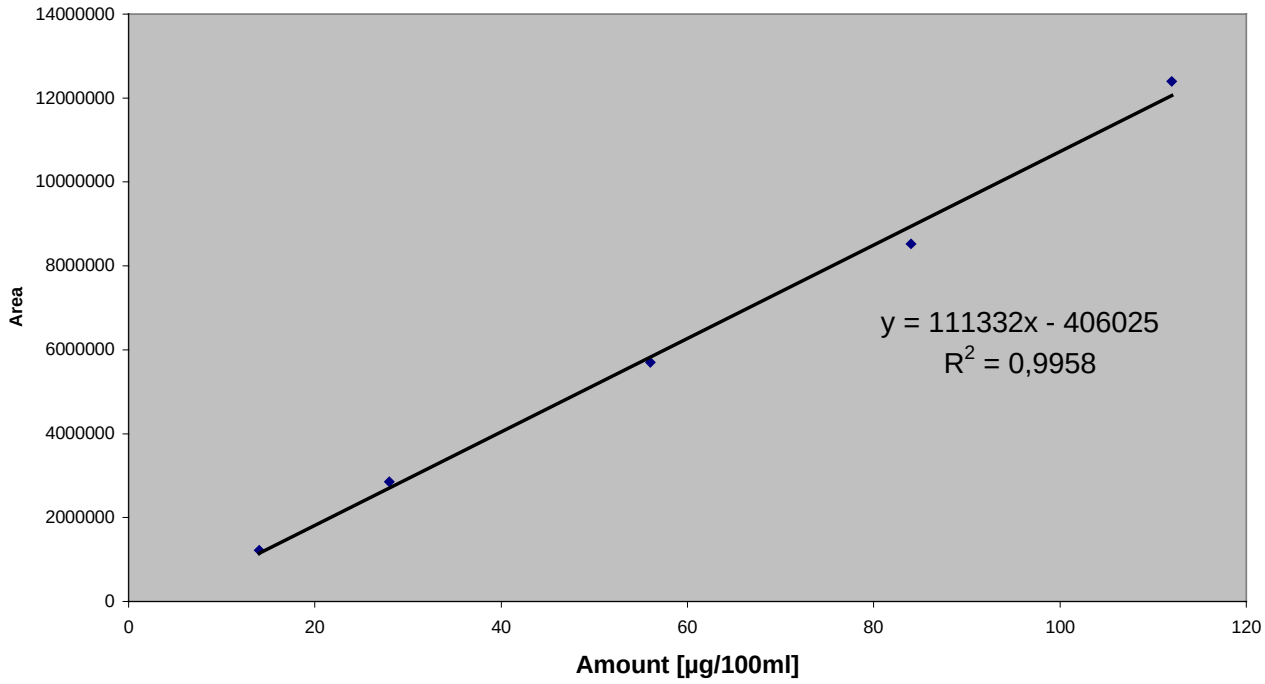
Bis (2-ethylhexyl) azelate



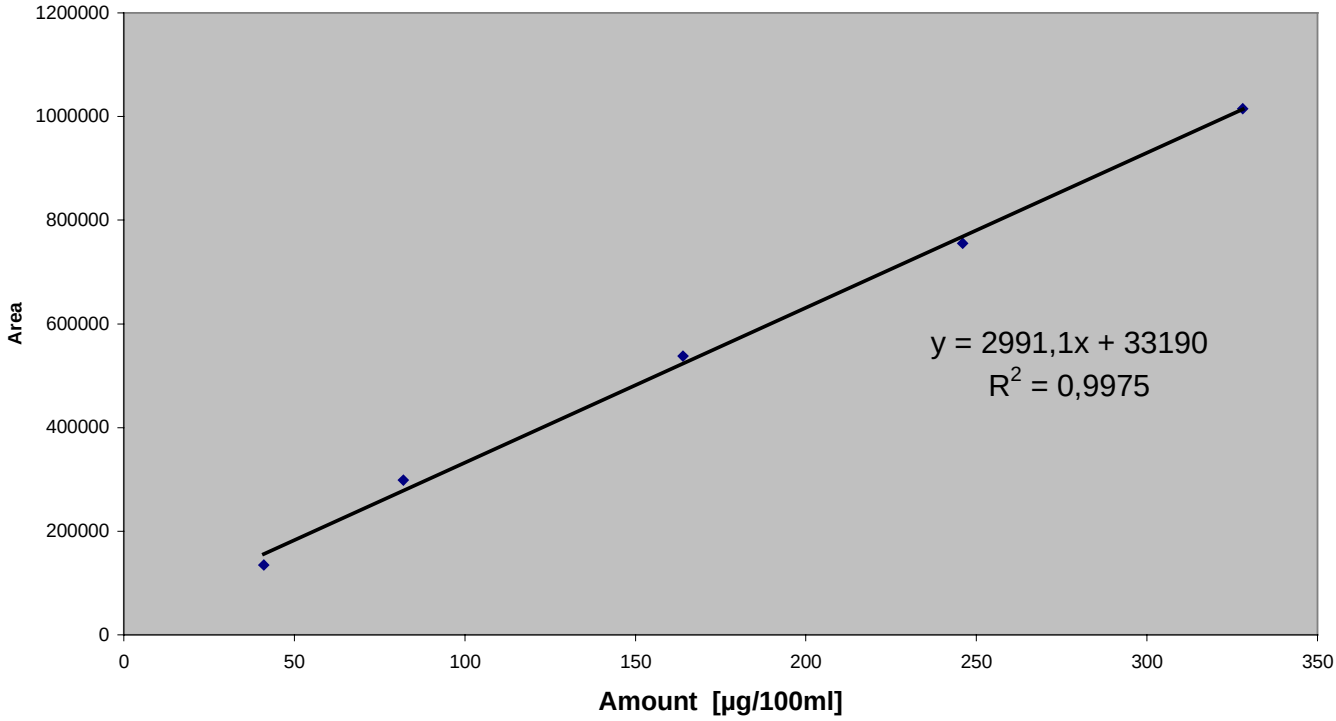
Diisodecyladipat



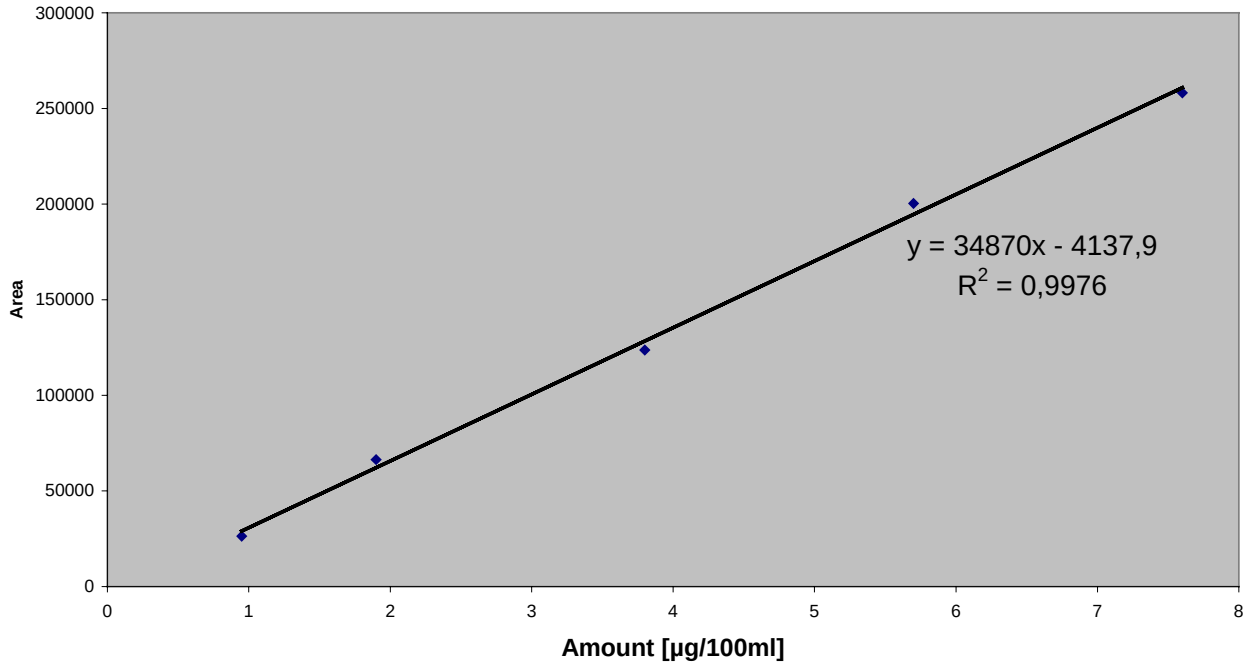
Diisononyl phthalate



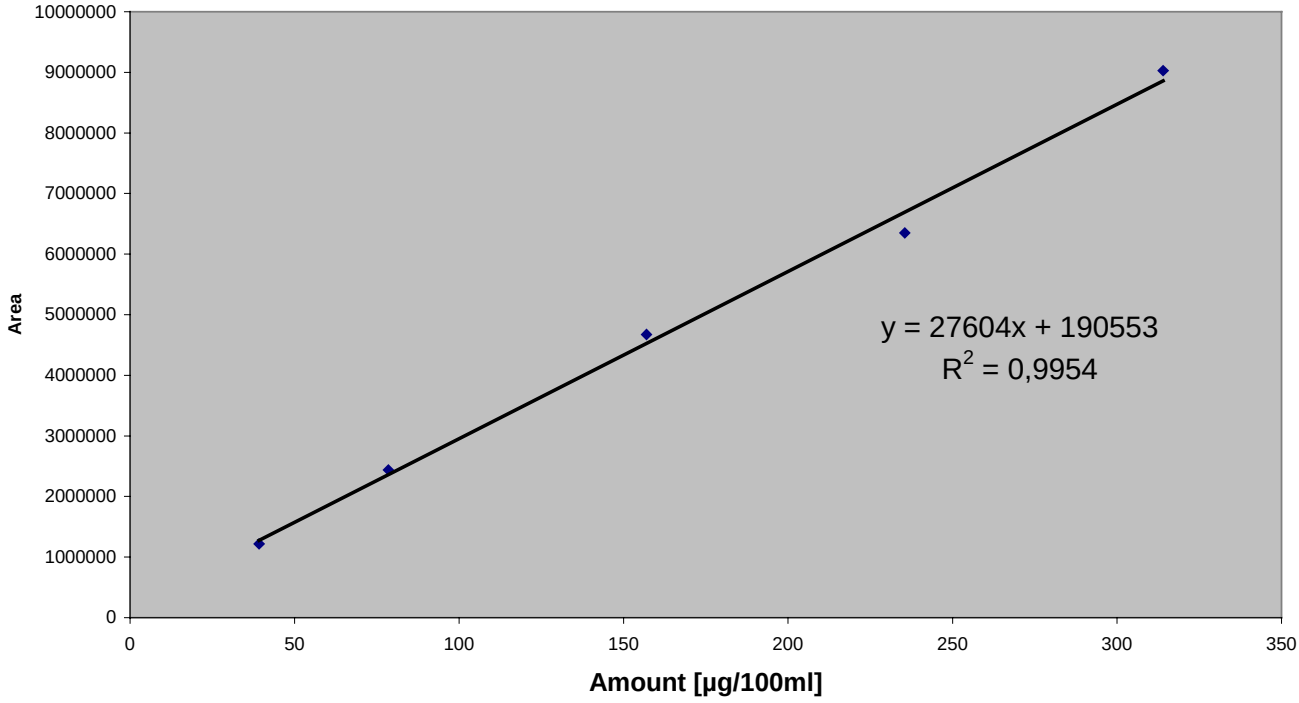
Bis [2-(2-butoxyethoxy) ethyl] adipate



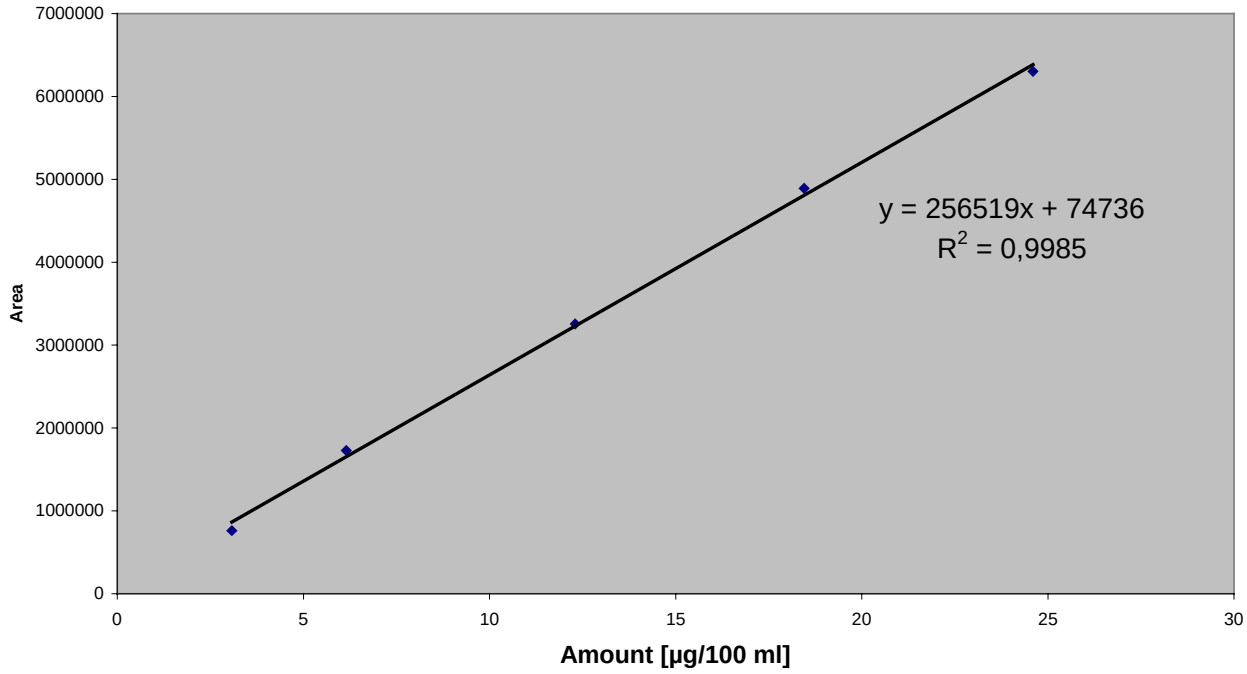
Triphenylphosphat



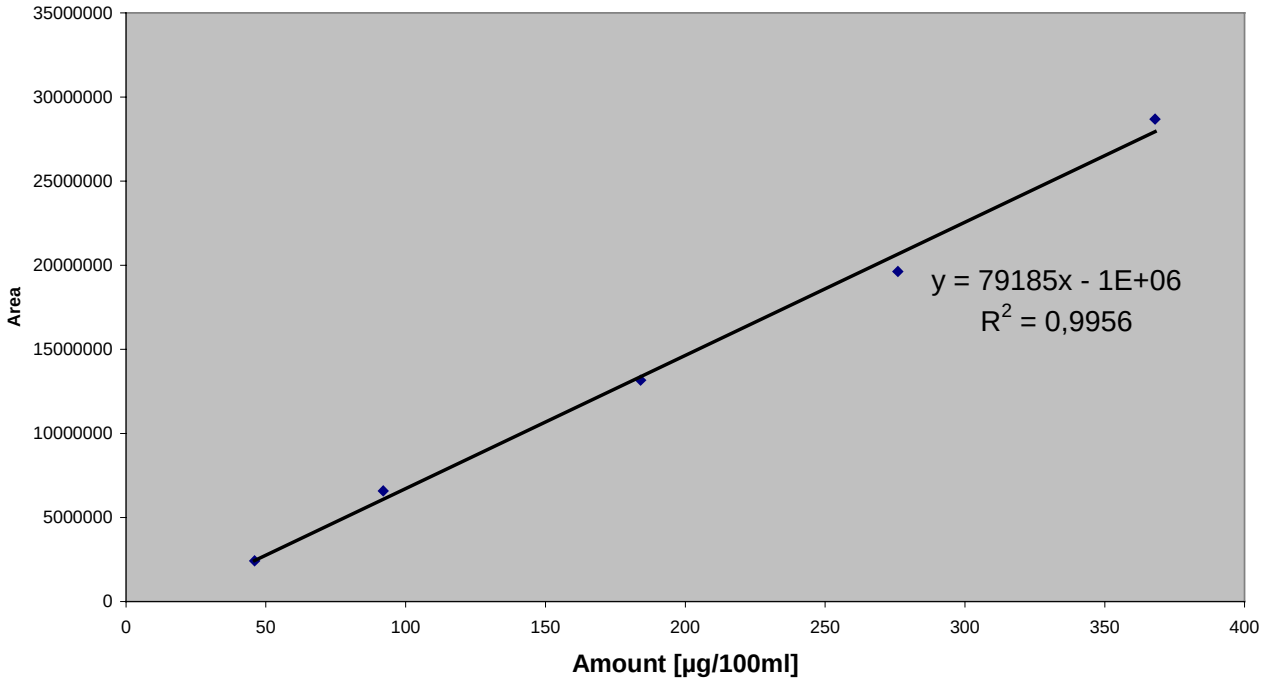
Tributyl o-acetyl citrate



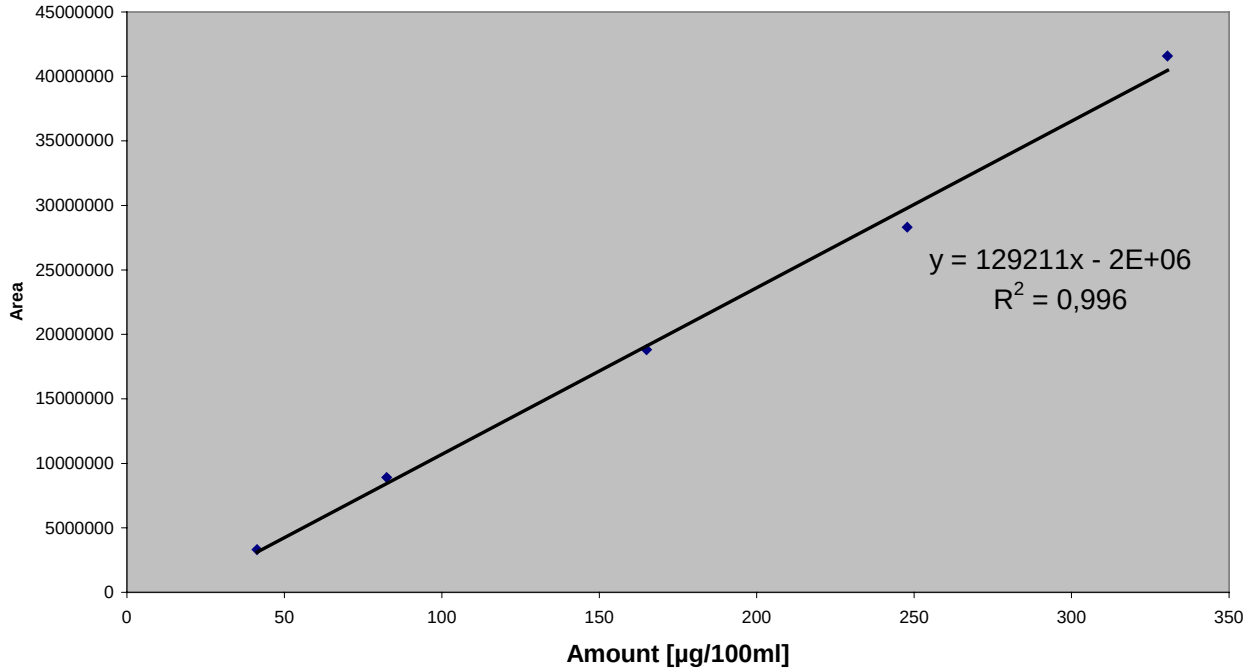
Bis (2-ethylhexyl) phthalate



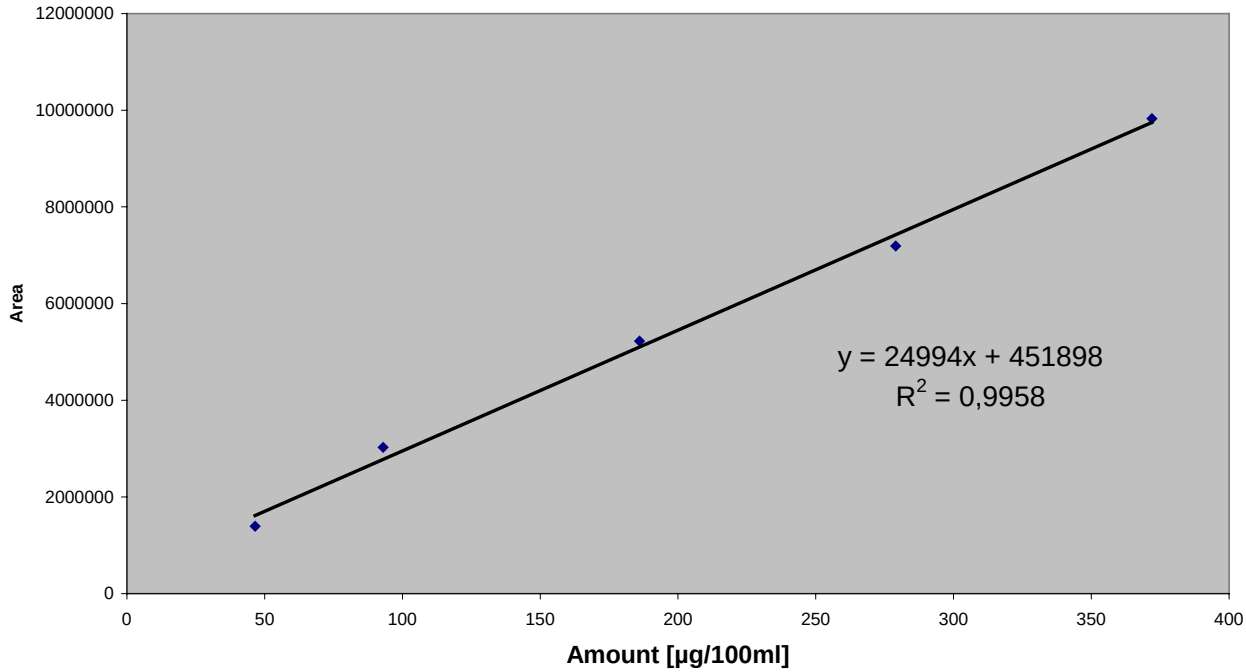
Tributylphosphat



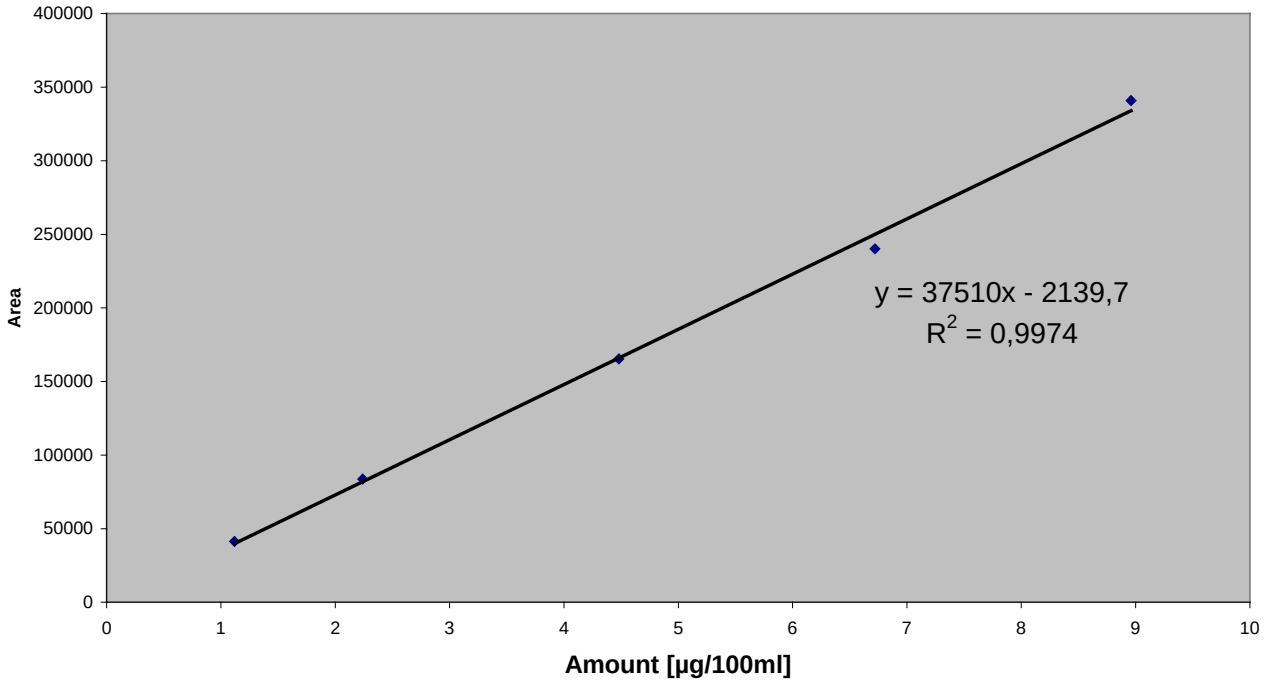
Di (ethylenglycol) dibenzoate



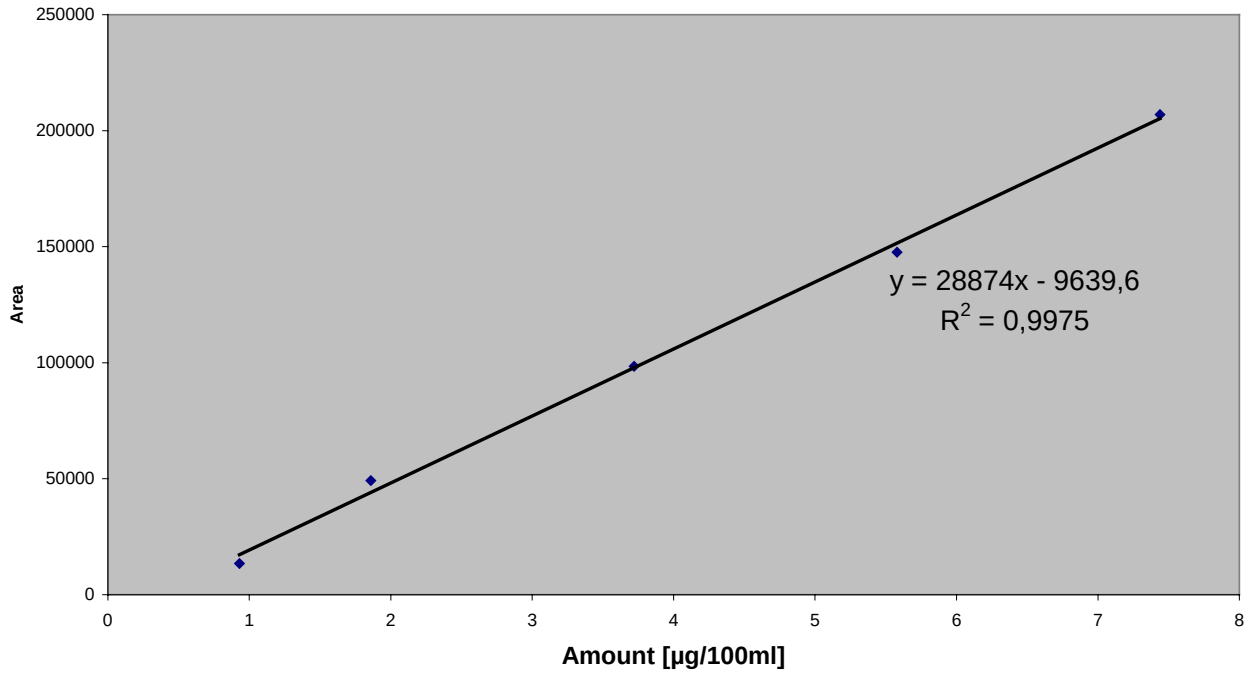
Di (propylengycol) dibenzoate

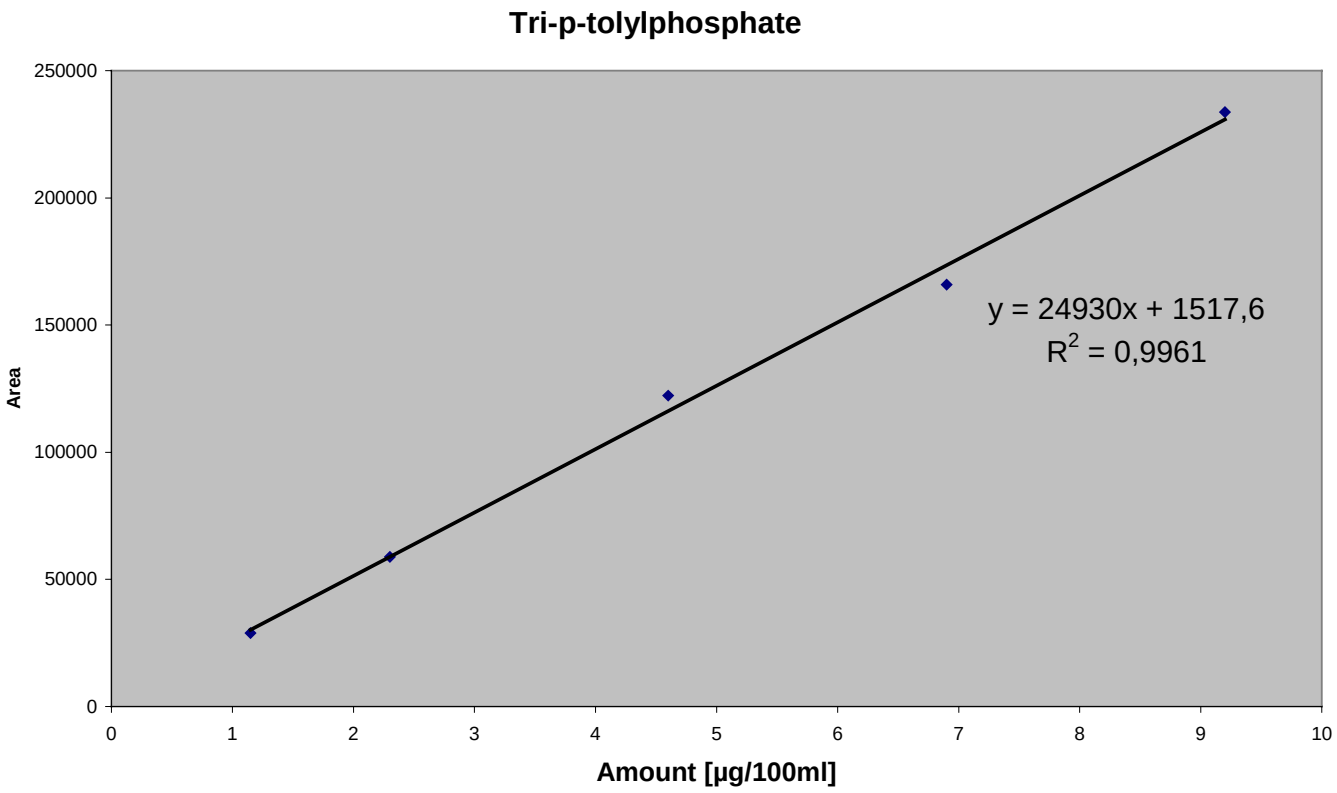


Tri-o-tolyphosphate



Tri-m-tolylphosphate




Tri-p-tolylphosphate
250000
200000
150000
100000
50000
0
Area
0
1
2
3
4
5
6
7
8
9
10
Amount [µg/100ml]
y = 24930x + 1517,6
R2 = 0,9961

Annex D Normative requirements for priority 1 plasticizers

1. Scope

This method describes the analysis of plasticizers in aqueous solution (obtained by extraction of toy samples with water) using liquid/liquid extraction and GC/MS analysis. The plasticizers as well as the validated concentration ranges are indicated in the table below.

Substance	**CAS**	**in 100ml H_2O**
Triphenyl phosphate	115-86-6	3,0 - 24µg
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	3,0 - 24µg
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	3,0 - 24µg
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	3,0 - 24µg

2. Principle

An aqueous solution of plasticizers is subjected to a single extraction using toluene:ethylacetate 95:5 in a separatory funnel. The concentrations are determined by GC/MS in SIM-mode using a non-polar column. For quantification both external and internal standards are used.

3. Chemicals

3.1 Solvents

3.1.1

Acetone, analytical grade or equivalent

3.1.2

Toluene, analytical grade or equivalent

3.1.3

Ethylacetate, analytical grade or equivalent

3.1.4

Solvent Mixture: Mixture containing 95%-vol toluene and 5%-vol ethylacetate

3.1.5

Water deionized, PH 6-8

3.2 Plasticizers

Substance	Purity according to manuf.	CAS-Nr.	Manufacturer
Triphenyl phosphate	>98%	115-86-6	Fluka
Tri-*o*-tolyl phosphate	98%	78-30-8	Chem Service
Tri-*m*-tolyl phosphate	97%	563-04-2	Acros
Tri-*p*-tolyl phosphate	>98%	78-32-0	Acros

or equivalent from other producers

3.3 Other

3.3.1

Benzylbutyl phthalate (internal standard)

4. Apparatus

Gaschromatograph: HP5890 Series II or equivalent

Analytical column: Optima delta-3 (manufacturer: Macherey & Nagel, Germany), dimensions: 30m*0,25mm*0,25µm, or equivalent

Autoinjector: HP7673A equipped with a 10µl syringe fast injection mode or equivalent (or handheld syringe)
Split/Splitless-injector at constant pressure or equivalent, split flow 10ml/min, split injection
Injection volume: 1µl
Pressure: 150kPa Helium (Purity: 99,999% or better)
Septum purge flow: 2ml/min
Inlet temp.: 275°C

Oven temp. progr.: Init Temp.: 100°C
Init Time: 1min
Rate: 7°C/min
Final Temp.: 300°C
Final Time: 10min

Slight deviations are acceptable provided the peak resolution is sufficient (Rs $\geq$ 1,5)

Transfer-Line Temp.: 290°C

Mass selective Detector: HP5970B or equivalent

Software: G1701AA Rel. A03.00 or equivalent for data processing

Single Ion monitoring: For each substance two ions are used for quantification: typically the base ion as target ion and the ion with the second highest peak in the mass spectrum as qualifier. In the case of interference with other substances other ions are chosen. The target ion is used for quantification, the qualifying ion is used for positive identification of the substance. The use of a qualifier ion reduces the risk of false positive results due to interfering signals. A deviation of 20% from the expected response of the qualifier ion is acceptable.

List of target and qualifier ions for plasticizers:

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Triphenyl phosphate	115-86-6	325	169
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	165	179
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	368	165
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	368	165

Target and qualifier ions for internal standard

Substance	**CAS Number**	**Target Ion**	**Qualifier**
Benzylbutyl phthalate (Internal Standard)	85-68-7	149	206

Time windows of monitored ions:

Start time [min]	Monitored ions [amu]
27	149, 206
29	325, 169
31	165, 179, 368

Glass separatory funnels 250ml with glass stopper and teflon faucet
Volumometric glassware (pipettes, measuring cylinders, flasks)
Pipette 50µl

Vials for autosampler
Usual laboratory equipment

5. Procedure

5.1 General

Rinse all glass ware and other items in contact with the sample or standard solutions twice with acetone.

5.2 Stock solutions

A stock solution in acetone is prepared containing benzylbutyl phthalate to the nearest of 10mg/ml (Stock solution Istd1). Prepare a dilution 1:10 in acetone to obtain a concentration of 1mg/ml (Stock solution Istd2).

A stock solution in acetone is prepared containing all plasticizers to the nearest of the following concentration levels (Stock solution P):

Substance	Concentration [mg/ml]
Triphenyl phosphate	0,12
Tri-*o*-tolyl phosphate	0,12
Tri-*m*-tolyl phosphate	0,12
Tri-*p*-tolyl phosphate	0,12

5.3 Calibration standards

Dilute stock solution P to obtain calibration standards at the 200%, 150%, 100%, 50% and 25% level of the concentrations given below. Use toluene as a solvent.

Calibration standard 100%:

Substance	CAS Number	in 1ml toluene
Triphenyl phosphate	115-86-6	1,2µg
Tri-*o*-tolyl phosphate, tri-*o*-cresyl phosphate	78-30-8	1,2µg
Tri-*m*-tolyl phosphate, tri-*m*-cresyl phosphate	563-04-2	1,2µg
Tri-*p*-tolyl phosphate, tri-*p*-cresyl phosphate	78-32-0	1,2µg

Add stock solution Istd (benzylbutyl phthalate in acetone; c=10mg/ml) as internal standard to obtain a internal standard concentration of 5µg/ml. This can be achieved, e.g. by adding 50µl of the stock solution Istd1 to 100ml of the diluted stock solutions.

5.4 Sample extration

Prepare a blank by adding 50µl of stock solution Istd1 of benzylbutyl phthalate in acetone (c=10mg/ml) to 1l of deionized water.

Add 50µl of stock solution Istd2 of benzylbutyl phthalate in acetone (c=1mg/ml) to 100ml water sample.

100ml of the blank or water sample are extracted with 10ml of the solvent mixture containing 95%-vol toluene and 5%-vol ethylacetate by shaking in a 250ml separatory funnel for 1 minute. Let the two phases set apart and draw off the upper layer.

5.5 Analytical determination

Analyse each calibration standard, blank and sample following the conditions defined in clause 4.

After data collection is complete establish calibration curves using the appropriate target and qualifier ions. The internal standard should be used. Correlation coefficient should be better than 0,995 for a linear calibration function. If not, use a 2^{nd} order calibration function.

Determine plasticizer content in the samples by using these calibration curves.

Content of plasticizers determined in blank should not exceed 10% of the content in the lowest calibration standard.

Annex E Literature search

1. Introduction

This report on a literature search is intended to provide information on available methods of analysis for the determination of plasticizers other than phthalates potentially used in toys. The work has been carried out in the framework of the development of European standards dealing with organic chemicals in toys carried out by CEN TC 52 “Safety of toys” following a mandate by the European Commission.

2. Substances requiring methods of analysis

The members of CEN have notified a total of 33 chemicals used as plasticizers to be considered for incorporation in the future European toys standard. These substances are given in document CEN/TC 52/WG9/TG2/N94rev2 and are listed in table 1 below.

At the time of production of this report the substances were subject of assessment by a group of toxicologists (CEN TC 52 WG9 TG3) which was requested to to identify plasticizers of concern and to propose appropriate limit values. In order not to lose time it has been decided to cover all of the listed chemical compounds by the literature study although it is expected that some of them will be eventually excluded.

Table 1: Plasticizers requiring methods of analysis.

8.1.1.3 Substance	**CAS Number**
Tributyl O-acetylcitrate	77-90-7
Tributyl citrate	77-94-1
Triethyl O-acetylcitrate	77-89-4
Triethyl citrate	77-93-0
Tris(2-ethylhexyl) O-acetylcitrate	144-15-0
Tris(2-ethylhexyl) citrate	7147-34-4
Bis(2-butoxyethyl) sebacate	141-19-5
Bis(2-ethylhexyl) sebacate	122-62-3

Dioctyl sebacate	2432-87-3
Trialkyl(C7-C9) trimellitate	68515-60-6
Triisooctyl trimellitate	27251-75-8
Trioctyl trimellitate	89-04-3
Bis[2-(2-butoxyethoxy)ethyl] adipate	141-17-3
Bis(2-butoxyethyl) adipate	141-18-4
Bis(2-ethylhexyl) adipate	103-23-1
Dialkyl(C7-C9) adipate	68515-75-3
Didecyl adipate	105-97-5
Diisodecyl adipate	27178-16-1
Dioctyl adipate	123-79-5
Bis(2-ethylhexyl) azelate	103-24-2
Dioctyl azelate	2064-80-4
Diisooctyl azelate	26544-17-2
Triphenyl phosphate	115-86-6
Tritolyl phosphate, tricresyl phosphate	1330-78-5
Tri-o-tolyl phosphate, tri-o-cresyl phosphate	78-30-8
Tri-m-tolyl phosphate, tri-m-cresyl phosphate	563-04-2
Tri-p-tolyl phosphate, ti-p-cresyl phosphate	78-32-0
Butyl benzoate	136-60-7
Diethylene glycol dibenzoate	120-55-8
Dipropylene glycol dibenzoate	94-51-9
Alkyl(C8-C18)sulfonic acids	
Bis(2-ethylhexyl) terephthalate	6422-86-2
Bis(2-ethylhexyl) isophthalate	137-89-3

3. Method of analysis

This report contains two appendices. The first one includes bibliographic data (title, author(s), source, and summary) of the literature found. The second appendix is a table in which relevant analytical information (sample preparation, chromatographic conditions, type of detector) for individual substances is given.

3.1. Sample Preparation

The plasticizers may have to be determined either from an aqueous solution following the procedures described in the draft standard “PartX: Organic chemical compounds – Sample preparation and extraction

procedures" (migration) or may have to be determined from an organic solution following extraction of the plastic material (totals) using a suitable solvent.

3.1.1. Extraction of aqueous solution

In previous studies the authors of this report used chloroform and dichloromethane to extract plasticizers (DEHP, DINP, DEHA, and ATBC) from water or (artificial) saliva. It could be shown that the extraction efficiency using these solvents was superior to hexane when DEHP was analysed (I. Steiner, L. Scharf, F. Fiala and J.Washüttl: Migration of di-(2-ethylhexyl) phthalate from PVC child articles into saliva and saliva simulant. Food Additives and Contaminants **7**, 812-817 (1998)).

Cyclohexane was chosen as solvent in the project: "Validation of methodologies for the release of diisononylphthalate (DINP) in saliva simulant from toys" co-ordinated by the Joint Research Centre (JRC) of the European Commission (EU report EUR198826 EN 2001). This solvent could be shown to be superior to dichloromethane, iso-octane and mixtures of hexane/diethylether. Hence, we suggest to conduct some comparison tests regarding extraction efficiency employing dichloromethane and cyclohexane.

3.1.2. Extraction of plastic material

There are in principle two options to determine the content of plasticizers in plastic materials:

- a soxhlet extraction
- dissolution followed by precipitation of the plastic by addition of another solvent

The general strategy for the extraction is to find a solvent in which the plasticizer is readily soluble whereas the polymer is not. Typically diethylether has been used to determine low molecular plasticizers (phthalates, adipates, azelates, sebacates, citrates, phosphates, esters of sulphonic acids and others) in PVC [Wandel et al., 11-GC].

In the dissolution/precipitation approach the idea is to dissolve the polymer including the plasticizer in a a first step. Subsequently a second solvent is added to precipitate the polymer whereas the plasticizer remains in solution. Unsoluble plastic material can be separated by using a centrifuge or a filter. Tetrahydrofurane (THF) or cyclohexanone have been frequently used to dissolve PVC. Methanol, ethanol and hexane are typical precipitation solvents. Direct injection of the tetrahydrofurane solution without precipitation has been done as well [Krishen, 6-GC].

In the JRC report mentioned above on the validation of the DINP method it is reported that the dissolution/precipitation method using THF and hexane gave better results compared with a 6-hours soxhlet extraction using diethylether. Furthermore, a "slow overnight dissolution method at ambient temperature" was claimed to be superior to a "fast dissolution method using ultrasound". However, no details are given.

We conclude that some tests will have to be carried out to determine the best option for those plasticizers for which a total limit is to be set.

3.2. Analytical determination

Table 2 summarises the findings of the literature search with respect to the analytical techniques applicable to the listed substances. As can be gathered from table 2 the large majority of the plasticizers in question can be determined by employing gas chromatography. However, some substances of low volatility (e.g. trimellitates) can only be analysed by HPLC. For several plasticizers both options are possible.

Table 2. Chromatographic techniques found in literature for the different plasticizers.

Substance	**Technique**
Tributyl O-acetylcitrate	GC/MS; GC/FID; HPLC/RI
Tributyl citrate	GC/FID
Triethyl O-acetylcitrate	GC/FID
Triethyl citrate	GC/FID
Tris(2-ethylhexyl) O-acetylcitrate	GC/FID
Tris(2-ethylhexyl) citrate	------
Bis(2-butoxyethyl) sebacate	GC/FID
Bis(2-ethylhexyl) sebacate	GC/FID
Dioctyl sebacate	GC/MS; GC/FID; HPLC/UV; HPLC/RI
Trialkyl(C7-C9) trimellitate	HPLC
Triisooctyl trimellitate	HPLC
Trioctyl trimellitate	HPLC
Bis[2-(2-butoxyethoxy)ethyl] adipate	GC/MS; GC/FTIR
Bis(2-butoxyethyl) adipate	GC/MS; GC/FTIR
Bis(2-ethylhexyl) adipate	GC/MS; GC/FTIR; GC/FID; HPLC/UV; HPLC/RI
Dialkyl(C7-C9) adipate	HPLC/RI
Didecyl adipate	GC/MS; GC/FTIR; GC/FID
Diisodecyl adipate	GC/MS; GC/FTIR; GC/FID; HPLC/UV; HPLC/RI
Dioctyl adipate	GC/MS; GC/FTIR; GC/FID; HPLC/UV; HPLC/RI
Bis(2-ethylhexyl) azelate	GC/FID
Dioctyl azelate	GC/MS
Diisooctyl azelate	GC/FID
Triphenyl phosphate	GC/MS; GC/PND; GC/FID; HPLC/UV

Tritolyl phosphate, tricresyl phosphate	GC/PND; GC/FID; HPLC/UV; HPLC/RI
Tri-o-tolyl phosphate, tri-o-cresyl phosphate	GC/FID; HPLC/UV
Tri-m-tolyl phosphate, tri-m-cresyl phosphate	GC/PID
Tri-p-tolyl phosphate, ti-p-cresyl phosphate	GC/PID
Butyl benzoate	GC/FID
Diethylene glycol dibenzoate	GC/FID; HPLC/UV
Dipropylene glycol dibenzoate	GC/FID; HPLC/UV
Alkyl(C8-C18)sulfonic acids	GC/MS; GC/FID; HPLC/UV; HPLC/Conductivity; HPLC/Florimeter
Bis(2-ethylhexyl) terephthalate	HPLC/UV; HPLC/RI
Bis(2-ethylhexyl) isophthalate	GC/FID

In the following some additional remarks pertaining to the various plasticizer groups are made:

Citrates:

Several publications were found which describe the separation and identification of all listed citrates with the exception of tris (2-ethylhexyl) citrate using GC. According to Wandel et al [11-GC] several acetylated citrates do not differ significantly from non-acetylated citrates in terms of gas chromatographic retention times. It is likely that tris (2-ethylhexyl) citrate shows a similar GC behaviour to (2-ethylhexyl) O-acetylcitrate. For the latter substance GC data have been reported. This means that GC is the method of choice for all citrates listed in tables 1 and 2.

Sebacates:

For all listed sebacates GC data could be found in literature. In addition, Patuska et al. [2-HPLC] have reported HPLC data for dioctyl sebacate.

Trimellitates:

Trimellitates cannot be analysed by GC because of decomposition during evaporation. They are determined by using HPLC. Normally reversed phase columns are used to this end. Groß et al. [1-HPLC] and Kelm et al. [3-HPLC] have reported the separation of technical mixtures C6-C10 and C8-C10, respectively. We could not find any details regarding C7-C9 trimellitates. It should be clarified how to proceed in case a different mixture is found (not C7-C9 but C6-C10 and C8-C10). Should the pattern be evaluated or individual compounds (peaks)? This is, of course, only relevant if trimellitates are included in the final list.

Adiates:

Adipates and in particular bis (2-ethylhexyl) adipate) have been more frequently analysed than other plasticizers. Guisto et al. [10-GC] presented retention indices of 17 industrially important adipate esters, along with mass and infrared spectra of some of these substances. All adipates listed in tables 1 and 2 with the exception of dialkyl(C7-C9) adipate are included in the paper.

As far as the latter is concerned the same question needs to be raised as in the case of the technical mixture. Is just the specific mixture of interest or are the individual components in the given range also relevant? Clarification is needed on this issue.

Azelates:

GC data were found for all 3 listed azelates.

Phosphates:

Triphenyl phosphate and tritolyl phosphate have been investigated by means of GC and HPLC.

Tritolyl phosphate exists in three isomeric forms: ortho, meta and para. The technical mixture contains mainly the meta and the para isomers and low levels of the highly toxic ortho isomer. All three isomers can be separated by GC. At present both the mixture and the isomers are listed in document N94rev2 which is confusing. It is suggested to eliminate the mixture and to refer to the individual isomers only.

Benzoates:

Butylbenzoate has been determined by GC. A mixture of diethylene glycol dibenzoate und dipropylene glycol dibenzoate have been separated by using GC and HPLC in a theses carried out at the Institute of Food Chemistry and Technology at the Vienna University of Technology [5-HPLC]=[18-GC]. Also in this case we would go for the GC method.

Alkylsulfonic acids:

The analysis of alkylsulfonic acids is complicated. A GC determination is only possible after derivatisation (e.g. trimethylsilyl derivatives or methyl esters). Due to the lack of a chromophor the detection of alkylsulfonates by using HPLC is not easy either (the direct use of UV detection is not possible). Various methods have been developed to overcome this problem including indirect photometric detection, post-column transformation of sulfonates, ion pair formation and so forth.

It is impossible to develop a general method for all C8-C18 alkysulfonic acids in the framework of this project because all 11 sulfonic acids would have to be evaluated individually which would be an enormous amount of work. It is therefore suggested to identify the sulfonic acids which are of real concern. In case those are contained in the final list we would go for a GC analysis following derivatisation.

Terephthalates und Isophthalates:

Publications on terephthalates and isophthalates are scarce. Only one method was found for each of the substances (a HPLC method for bis (2-ethylhexyl) terephthalate and a GC method for bis (2-ethylhexyl) isophthalate). We will try to determine both by using GC.

5. Conclusion

It is suggested to develop a GC/MS method for the separation and detection of plasticizers pertaining to the substance families citrates, sebacates, adipates, azelates, phosphates benzoates, terephthalates (if possible) and isophthalates. It is estimated that 29 out of 33 substances could be covered by the method. A capillary column of low polarity and high temperature resistance will be chosen (e.g. DB-1 or DB-5 or equivalent).

The remaining trimellitates and the terephthalate (if not possible with GC/MS) could be covered by a reversed phase HPLC method as well as other plasticizers in case the GC/MS method turns out to be difficult or does not give satisfactory results.

Further clarification is needed with respect to alkyl sulfonic acids. The relevant substances should be identified for incorporation in the study. A GC method following derivatisation could be developed for these alkyl sulfonic acids.

Some clarification is also needed with respect to the technical mixtures trialkyl (C7-C9) trimellitate and dialkyl (C7-C9) adipate as outlined in the text.

Finally, it is suggested to delete tritolyl phosphate because of redundancy. The ortho, meta and para isomers are listed anyway.

Appendix 1. Literature search Plasticizers.

Filename : [1-GC]
Title : DETERMINATION OF PLASTICIZERS IN FOOD BY GAS-CHROMATOGRAPHY-MASSSPECTROMTRY WITH ION-TRAP MASS DETECTION

Author(s) : Oi-Wah Lau, Siu-Kay Wong
Publication : Journal of Chromatography A, 737 (1996), 338-342.
Summary : In this paper a method for the determination of plasticizers in food by gas chromatography-mass spectrometry with ion-trap mass detection is described. The plasticizers were quantified by an internal standard addition method using diisobutyl phthalate as the internal standard. Four selected food samples were spiked with nine different plasticizers at about 0.3 μg/g. The recoveries of the plasticizers were in the range of 90 to 106%. The proposed method shows an improvement in precision and exhibits good linearity over a wide concentration range. The new method was applied to the analysis of real samples and the results were found to agree with those obtained using the well-established isotope dilution technique.

Filename : [2-GC]
Title : GAS-LIQUID CHROMATOGRPHIC RETENTION INDICIES OF 296 NON-DRUG SUBSTANCES ON SE-30 OR OV-1 LIKELY TO BE EN-COUNTERED IN TOXICOLOGICAL ANALYSES

Author(s) : John D. Ramsey, Terence D. Lee, M. David Osselton, Anthony C. Moffat
Publication : Journal of Chromatography, 184 (1980), 185-206.
Summary : The advent of the widespread use of selective detectors (electron capture detector, phosphorus/nitrogen detector) for gas-liquid chromatography used in toxicological analyses has revealed the presence of hitherto unseen interfering materials. These substances may be conveniently grouped into (1), anti-oxidants; (2), putrefactive and endogenous compounds; (3), pesticides; (4), food additives, flavours and fragrances, (5) plasticizers, plastic additives and vulcanising agents and (6), scintillation reagents. To facilitate the identification of these materials, retention indices on the dimethyl silicon phase SE-30 or OV-1 have been compiled by the two laboratories to include 296 such compounds. Most gave single peaks, but some gave complex patterns indicating that they

were mixtures of compounds. Of the 296 compounds, 14 did not give observable peaks, 8 gave 2 or 3 peaks and 44 gave more than 3 peaks. To determine the interlaboratory difference between retention index measurements, 17 compounds were chromatographed by both laboratories: the mean difference was ± 13 retention index units with only one greater than ± 50 retention index units. Examples of how these materials may be encountered during toxicological analyses are given. Data are also presented on compounds, which have been used as internal standards.

Filename : [3-GC]
Title : GASCHROMATOGRAPHISCHE IDENTIFIZIERUNG VON WEICH-MACHERN IN KUNSTSTOFFEN

Author(s) : M. Gillio-Tos, A. Vimercati
Publication : Kunststoffe Bd. 36. 1966 Heft 6, 409-412.
Summary : The separation and gas chromatographic identification of a large number of plasticizers, which are primarily used for homo and copolymers of vinyl chloride, are described. Some of the examined plasticizers cannot be separated by gas chromatography. With the help of additional methods of analysis including IR-spectroscopy, and thin-layer chromatography as well as some chemical reactions, it is possible to identify these plasticizers. The quantitative determination of the plasticizers is also possible with help of the gas chromatography.

Filename : [4-GC]
Title : CHROMATOGRAPHISCHE VERFAHREN ZUR IDENTIFIZIERUNG VON WEICHMACHERN. ANALYSE VON CITRONENSÄURE- UND SEBACIN-SÄUREESTERN (CHROMATOGRAPHIC IDENTIFICATION OF PLASTICIZERS: ANALYSIS OF CITRIC ACID ESTERS AND SEBACIC ACID ESTERS)

Author(s) : M. Wandel, H. Tengler
Publication : KUNSTSTOFF-RUNDSCHAU(1965), 12 (10), 559-64.
Summary : Plasticizers are separated by extraction of the crushed sample for 6-8 hours with ether, followed by evaporation of the solvent. A spot test on sebacates (I) and citrates (II) is carried out: 2 drops of the plasticizer are heated with resorcinol and 1-2 drops concd. H_2SO_4 at 160° for 30-60 sec. After cooling, H_2O is added, the solution rendered alkalish with 10% NH_4OH, and diluited with H_2O to 150 ml. (I) shows a yellow colour and yellow-yellow-green fluorescence in UV light. (II) shows an orange colour and light-blue fluorescence with UV. Blanks are run for comparison. Qual. investigation was carried out by thin-layer chromatography (TLC) by using sillica gel G which was prepared with

Blankophor DCB. The spots were made visible with UV light. Thus, 1g Blankophor DCB is dissolved in 40 cc. Me_2CO, the solution filtered, the filtrate mixed with a suspension of 30 g silica gel G in 40 cc. Me_2CO, and plates are coated with this mixture. After air drying, the plates are activated at 130°. CH_2Cl_2 or a mixture of iso-Pr_2O and petroleum ether (40-60°) in the ratio of 30:70 was used as eluent. Tri-Et, tri-Bu, tris(2-ethylhexyl), O-acetyl tri-Et, O-acetyl tri-Bu, and O-acetyl tris(2-ethylhexyl) citrate were separated from the mixture. Mixtures of di-Me, di-Et, di-Bu, bis(2-thylhexyl), and dibenzyl sebacate were also tested by TLC. Accurate identification by this method is difficult. For analysis by gas chromatography, the Me esters were prepared by transesterification at 130°C with p-$MeC_6H_4SO_3H$ as catalyst, and the reaction mixture was directly applied. Operating conditions, column length and diam., and packing materials are given. Resoflex LAC-2R-446, Ultramoll III, each on diatomaceous earth, and 5% silicone rubber GE SE-30 on Chromosorb were used. Quantitative analysis is possible (Wandel and Tengler, CA 61, 11057 e).

Filename : [5-GC]
Title : QUALITATIVE AND QUANTITATIVE GAS CHROMATOGRAPHIC DETERMINATION OF PLASTICIZERS IN POLYVINYL CHLORIDE

Author(s) : Jytte Lerche, J⌀rgen M⌀rch
Publication : Arch. Pharm. Chemi Sci. Ed. 1 (1973), 25-30.
Summary : A gas chromatographic method suitable for qualitative and quantitative determination of ester plasticizers in PVC has been developed. The method has been tested on PVC articles, intended primarily for pharmaceutical purposes; for example, drug containers, suppository moulds, blood-packs, and some tubing commonly used in medical utensils. The drug containers and the suppository moulds analysed did not contain any plasticizers, while the blood-packs and the tubing contained up to 45 per cent plasticizers. These were esters of phthalic, adipic, and citric acid.

Filename : [6-GC]
Title : PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY FOR IDENTIFICATION OF ESTERS PLASTICIZERS

Author(s) : Anoop Krishen
Publication : Analytical Chemistry (1971), 43(8), 1130-2.

Summary : The programmed temperature gas chromatographical conditions used to chromatograph plasticizers for plastics and their alcoholic and acidic components, and the relations of the relative retention to the carbon number were useful in identifying ester plasticizers. The acid components were identified by inference from the relative retention of the original plasticizers, and that of the alc. formed on hydrolysis. Similarly, the epoxidized vegetable oil plasticizers were identified through their Me ester derives. Two stainless steel columns packed with 10% UCW-98 on 60-80 mesh Diatoport S were used in a dual operational mode.

Filename : [7-GC]

Title : APLICATION DES CHROMATOGRAPHIES SUR COUCHE ET GAZ-LIQUIDE À L'ANALYSE QUALITATIVE ET QUANTITATIVE DES ESTERS DES ACIDES ALIPHATIQUES DICARBOXYLIQUES (APPLICATION OF THIN-LAYER AND GAS-LIQUID CHROMATOGRAHY TO THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF ALIPHATIC DICARBOXYLIC ACID ESTERS)

Author(s) : P.J. Bloom

Publication : Journal of Chromatography, 115 (1975), 571-580.

Summary : Qualitative and quantitative analysis of aliphatic dicarboxylic acid esters is not easy. Thin-layer chromatography alone is ineffective, good results can be obtained by coupling gas-liquid and thin-layer chromatography.

Filename : [8-GC]

Title : TRENNUNG UND NACHWEIS VON PVC-WEICHMACHERN MIT HILFE PHYSIKALISCH- CHEMISCHER ANALYSENVERFAHREN (SEPARATION AND DETECTION OF PVC PLASTICIZERS WITH THE AID OF PHYSICO-CHEMICAL ANALYSIS METHODS)

Author(s) : W. Fischer, G. Leukroth

Publication : Plastverband (1996), 20(2), 107-13.

Summary : The capability of pyrolytic and high temperature gas chromatography as well a IR-spectroscopy in detecting and identifying poly (vinyl chloride) plasticizers (e. g. phthalates, sebacates, phosphates) was investigated. A number of analalytical methods had to be

combined and the separation of components with thin-layer chromatography as helpful. The pyrograms, IR spectra, and R_f values of a number of plasticizers were reproduced.

Filename : [9-GC]
Title : QUICK IDENTIFICATION AND ANALYSIS OF PLASTICIZERS IN PVC BY PROGRAMMED-TEMPERATURE GAS CHROMATOGRAPHY USING THE BEST STATIONARY PHASES

Author(s) : Djelloul Messadi, Jean-Maurich Vergnaud
Publication : Journal of Applied Polymer Science, 24 (1989), 1215-1225.
Summary : A quick and safe identification method is shown for plasticizers in PVC using programmed-temperature gas chromatography. Plasticizers were identified by their retention index values measured by using normal paraffins. Several stationary phases with quite different polarity are proposed: with silicone polymers (SE 30, OV 17, and QF 1) and a porous polymer such as Tenax. Operational conditions were optimised. The initial column temperature was chosen at a low value of 100°C with the first three phases and 180°C for the fourth. The best of temperature increase with time seemed to be 10°C/min. The calculation method for retention values (temperature, time, indices) was chosen just because it needed no approximation. Thermodynamic values for the solution of plasticizers were measured by using isothermal chromatography with all the stationary phases. Our method allows the analyst to optimise the operational conditions (solvent, percent, temperature) for chromatography, to solve his own problem by making use of a pocket computer. Quantitative analysis of plasticizers was obtained with good accuracy after a previous extraction and the addition of normal paraffin as internal standard.

Filename : [10-GC]
Title : GAS CHROMATOGRAPHIC RETENTION INDICES, MASS, AND INFRARED SPECTRA OF INDUSTRIALLY IMPORTANT ADIPATE ESTERS

Author(s) : R. Guisto, S.R. Smith, J.D. Stuart, J. Hubball
Publication : Journal of Chromatographic Science, 31 (1993), 225-230.
Summary : Adipate esters are increasingly being used in the production of a variety of consumer commodities. These esters are not biodegradable and their concentrations in the environment are steadily increasing. Gas chromatography/mass spectrometry (GC/MS)

and GC/Fourier transform infrared (FTIR) have proven to be powerful of adipate esters in environmental and related samples. The important distinction between the geometrical isomers Di(2-ethylhexyl) adipate and di-n-octyl adipate was made based on the temperature programmed retention indices obtained. Temperature programmed retention indices were reported for 17 industrially important adipate esters along with mass and infrared spectra for several of the adipate esters.

Filename : [11-GC]
Title : ABTRENNUNG VON WEICHMACHERN

Author(s) : Martin Wandel, Hubert Tengler, Hermann Ostromov
Publication : Die Analyse von Weichmachern, Springer Verlag Berlin (1967).
Summary : An overview about different possibilities of extraction of plasticizers from plastic. In this book, the qualitative analyses of the carbonic acids, adipates, azelates, sebacates, phthalates, phosphates, and citrates plasticizers with the help of gas chromatography and different columns is described.

Filename : [12-GC]
Title : IDENTIFICATION AND DETERMINATION OF PRIMARY PLASTICIZERS IN POLYVINYL CHLORIDE CALENDERD FORMULATIONS.

Author(s) : D. Thorburn Burns, W. P. Hayes, P. Steele
Publication : Journal of Chromatography , 103 (1975), 241-245.
Summary : A method has been developed for the rapid identification and determination of single primary and certain mixed plasticizers in PVC sheetings. Direct injection of THF solutions of sheet samples containing dibutyl phthalate as internal standards gave excellent quantitative results; Individual analysis can be completed in less than 1 hour.

Filename : [13-GC]
Title : CHROMATOGRAPHISCHE VERFAHREN ZUR IDENTIFIZIERUNG VON WEICHMACHERN. ANALYSE VON PHOSPHORSÄURE-ESTERN

Author(s) : M. Wandel, H. Tengler
Publication : Plastverarbeiter 16 (1965), 607-614.

Summary : Phosphoric acid esters are the frequently used plasticizers in the processing of polyvinyl chlorid, cellulose esters and other plastics. In this paper, the qualitative analyses of phosphoric plasticizers with the help of thin layer chromatography and gas chromatography is described. A qualitative and quantitative detection method of the plasticizers including its phenolic compounds is described.

Filename : [14-GC]
Title : DETECTION OF TRICRESYL PHOSPHATES AND DETERMINATION OF TRI-O-CRESYL PHOSPHATE IN EDIBLE OILS

Author(s) : Mahishi N.Krishnamurthy, S. Rajalashmi, Om Prakash Kapur
Publication : J. Assoc. Off. Anal. Chem. (1985), 68 (6), 1074-1076.
Summary : Tricresyl phosphate (TCP) in contaminated edible oils was extracted using acetonitrile and detected by thin layer chromatography as well as gas chromatography (GC). The chromatoplate was developed with isooctane-ethyl acetate (90 + 10) and visualized by spraying with 2,6-dichloroquinone chloroimide. TCP gives a characteristic blue-violet spot when heated at 100°C for 15 min. The method is direct and sensitive and can be used to detect as low as 2.5 μg TCP or TOCP (tri-o-cresyl phosphate). GC was carried out using 10% OV-101 as the stationary phase and flame ionisation detection for confirmation and quantitation of TOCP in oils.

Filename : [15-GC]
Title : TRIPHENYL PHOSPHATE ALLERGY FROM SPECTACLE FRAMES

Author(s) : Lars Carlsen, Klaus E. Andersen, Helge Egsgaard
Publication : Contact Dermatitis (1986), 15, 274-277.
Summary : A case of triphenyl phosphate allergy from spectacle frames is reported. Patch tests with analytical grade triphenyl phosphate, tri-m-cresyl phosphate, and tri-p-cresyl phosphate in the concentrations 5%, 0.5% and 0.05% pet. showed positive reactions to 0.05% triphenyl phosphate and 0,5% tri-m-cresyl phosphate, but no reaction to tri-p-cresyl phosphate. Gas chromatography of the tricresyl phosphate 5% pet. patch test material supplied from Trolab showed that it contained a mixture of a wide range of triaryl phosphates, including 0.08% triphenyl phosphate, which is above the threshold for detecting triphenyl phosphate allergy in our patient.

Filename : [16-GC]
Title : GAS-LIQUID CHROMATOGRAPHIC ANALYSES. XLII. RETENTION BEHAVIOR OF C1-C12 n-ALKYL ESTERS OF BENZOIC AND PENTAFLUOROBENZOIC ACIDS ON SE-30 AND OV-351 CAPILLARY COLUMNS

Author(s) : Ilpo O.O. Korhonen, Maija A. Lind
Publication : Journal of Chromatography, 328 (1985), 325-332.
Summary : The gas chromatographic separation of a mixture of C1-12 n-alkyl esters of benzoic and pentafluorobenzoic acids on low-polarity (E-30) and highly polar (OV-351) capillary columns is described. The Kovats' retention indexes for the fluorinated isomers are given. The results are compared with those reported by K. and L. (1985) for the corresponding n-alkyl benzoates by showing the retention index increments to the perfluoro substitution in the acyl chain at a variety of temps.

Filename : [17-GC]
Title : DISPERSION AND SELECTIVITY INDICES IN GAS CHROMATOGRAPHY III. ALKYL, ω-CHLOROETHYL AND ALKENYL BENZOATE AND CHLORO-BENZOATE ESTERS

Author(s) : M. B. Evans, J. K. Haken
Publication : Journal of Chromatography, 462 (1989), 31-37.
Summary : The dispersion (IM) and selectivity (I*) indices of homologous alkyl, ω-chloroethyl and alkenyl benzoate and monochlorobenzoate esters are presented as obtained on low polarity (SE-30) and polar (OV-351) capillary columns. The effects of alkyl chain length, un-saturation and the position of chlorination are discussed and the results compared with studies of aliphatic esters. The compounds considered allow a study of the effect upon retention of chlorination in both aromatic ring and the alkyl group.

Filename : [18-GC]=[5-HPLC]
Title : UNTERSUCHUNG ZUR MIGRATION VON ZUSATZSTOFFEN AUS PET-FLASCHEN IN OZONISIERTES TRINKWASSER

Author(s) : Elisabeth Richter
Publication : Thesis, Institute of Food Chemistry and Technology, Vienna University of Technology (1995).

Summary : Migration from additives into pet-bottles after ozonisation of drinking water is investigated. A mixture of plasticizers including Diethyleneglycol-dibenzoate and Dipropyleneglycol-dibenzoate is separated by gas chromatography and liquid chromatography. There are some problems with the choice of the right column and the temperature program. The substances can only be separated with a column resistant against high temperature (DEXIL 300 GC, up to 350°) because of their high boiling point.

Filename : [19-GC]
Title : GAS CHROMATOGRAPHIC METHOD FOR THE ASSAY OF ALIPHATIC AND AROMATIC SULPHONATES AS THEIR TERT.- BUTYLDIMETHYLSILYL DERIVATES

Author(s) : Lay-Keow NG, Michel Hupè
Publication : Journal of Chromatography, 513 (1990), 61-69.
Summary : A gas-liquid chromatography procedure is described which permits analysis of aliphatic and aromatic sulphonates as their tert-butyldimethylchlorosilane in acetonitrile. Stability results and mass spectral analysis of all. tert-butyldimethylsilyl sulphonates are presented. Each derivate displays a prominent and characteristic [M-57] fragment ion in is mass spectrum.

Filename : [1-HPLC]
Title : HOCHDRUCK-FLÜSSIGKEITSCHRMATOGRAPHIE- EINE ANALYS-ENMETHODE FÜR WEICHMACHER-GEMISCHE

Author(s) : D. Groß, K. Strauß
Publication : Kunststoffe 67 (1997) 8, 426-428.
Summary : Phthalates, phosphates and adipates and alkylsulfonates, acetyltributylcitrates, some sebacates, trimellitates and extenders used in plasticizers are investigated by high performance liquid chromatography (HPLC). Mixtures of strongly polar esters, aromatic phosphates and lower homologes can be separated using a silicone gel- column. Esters with high molecular alcohol compounds can be separated advantageous by application using a reversed phase-column and methanol-water-mixture as mobile phase.
Other plasticizers mixture are separated by a gradient elution. HPLC using a reversed phase- column is superior in the plasticizers analysis to the GC and DC.

Filename : [2-HPLC]
Title : CHROMATOGRAPHISCHE ANALYSE VON WEICHMACHERN (CHROMATOGRAPHIC ANALYSIS OF PLASTICIZERS)

Author(s) : G. Pastuska, U. Just, D. Barnheim
Publication : Kautschuk + Gummi, Kunststoffe (1983), 36, 479-81.
Summary : Plasticizers (phthalates, adipated, sebacates, phosphates, chloroparaffins) were analysed by high-pressure liquid chromatography (HPLC) and/or high-performance thin-layer chromatography (HPTLC). The retention time in HPLC of straight chain phthalate esters increased with the alcohol chain length (in HTPLC the migration distance increased). HPLC methods could not distinguish dinonyl phthalate from octyl phthalate.

Filename : [3-HPLC]
Title : IDENTIFIZIERUNG VON WEICHMACHERN (IDENTIFICATION OF PLASTICIZERS)

Author(s) : J. Kelm, H. Kretzschmar
Publication : Chromatographie/ Spektrometrie, GIT Supplement 4 (1986), 41-45.
Summary : Commercial plasticizers like phthalates, adipates, phosphates, trimellitates, alkylsulfonates and extenders are examined by High Resolution Liquid Chromatography and spectrometry. Reversed Phase is favoured for the separation of mixtures. The important methods for characterization and identification are IR-, NMR- and mass spectrometry. Applications of NMR are discussed in detail.

Filename : [4-HPLC]
Title : HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS ON RADIAL COMRESSION COLUMN OF THE NEUROTOXIC TRI-O-CRESYL PHOSHATE AND METABOLITES

Author(s) : Amin A. Nomeir, Mohamed B. Abou-Donia
Publication : Anaytical Biochemistry (1983), 135, 296-303.
Summary : A method utilizing high-performance liquid chromatography (HPLC) has been developed for the analysis of tri-o-cresyl phosphate (TOCP) and its possible metabolites, o-cresyl dihydrogen phosphate, di-o-cresyl hydrogen phosphate, o-hydroxybenzol alcohol, o-cresol, saligenin cyclic-o-tolls phosphate [2-(o-cresyl)-4-H-1:3:2:benzodioxaphosphoran-2-one], salicylic acid, salicylaldehyd, hydroxymethyl TOCP (di-o-cresyl o-hydroxymethylphenyl

phosphate), and hydroxymethyl TOCP (o-cresyl di-o-hydroxymethylphenyl phosphate). TOCP and its possible metabolites were analysed on a reverse-phase C18 cartridge fitted into RCM-100 radial-compression separation system. Compounds were separated using a linear gradient of 25 to 80% acetonitrile in 2% aqueous acetic acid at a flow rate of 1.3 ml/min in a period of 22 min. Quantification was achieved by monitoring the ultraviolet absorbance of the column eluates at 254 nm and measuring peak areas. Retention times and peak areas were highly reproducible for all compounds analysed. The relationship between peak area and amount injected was linear over a 100-fold range for o-hydroxybenzyl alcohol and salicylic acid, and 50 ng for the remaining compounds. A mixture of TOCP and its possible metabolites was added to samples of cat liver, kidney, and plasma and then extracted and analysed. High recovery and reproducibility for most compounds were observed in tissues analysed.

Filename : [5-HPLC]=[18-GC]
Title : UNTERSUCHUNG ZUR MIGRATION VON ZUSATZSTOFFEN AUS PET-FLASCHEN IN OZONISIERTES TRINKWASSER

Author(s) : Elisabeth Richter
Publication : Thesis, Institute of Food Chemistry and Technology, Vienna University of Technology (1995).
Summary : Migration from additives into pet-bottles after ozonisation of drinking water is investigated. A mixture of plasticizers including Diethyleneglycol-dibenzoate and Dipropyleneglycol-dibenzoate is separated by gas chromatography and liquid chromatography. There are some problems with the choice of the right column and the temperature program. The substances can only be separated with a column resistant against high temperature (DEXIL 300 GC, up to 350°) because of their high boiling point..

Filename : [6-HPLC]
Title : SPECTATOR ION INDIRECT PHOTOMETRIC DETECTION OF ALIPHATIC ANIONIC SURFACTANTS SEPARATED BY REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Author(s) : J.A.Boiani
Publication : Analytical Chemical 59 (1987), 2583-2586.
Summary : A simple technique is described for the detection of linear alkyl sulphate surfactants after separation by reversed-phase high-performance liquid chromatography. It makes use of

nonretained Inorganic absorber Ions and an ultraviolet detector. The optimum conditions for Isocratic and gradient elution are discussed and typical examples are given. The theoretical efficiency of the method is estimated. The technique is found to give linear responses for samples containing up to 100 μg of surfactant and has detection limits of 3-5 μg depending on sample type.

Filename : [7-HPLC]
Title : SEPARATION AND DETECTION OF NON-CHROMOPHORIC, ANIONIC SURFACTANTS

Author(s) : J.B. Li, P. Jandik
Publication : Journal of Chromatography 546 (1991), 395-403.
Summary : The newly developed Solid Phase Reagent (SPR) permits the conductivity detection of various alkylsulphonates and alkylsulphates. In its present version, SPR is an aqueous suspension of submicron particles of a polymeric cation exchange material in the hydrogen form. The SPR is pumped into the eluent stream coming from the separation column. The post-column reaction transforms the tetrabutylammonium alkyl sulphate or sulphonate into the corresponding free acid. This changes the analytes into more conductive species. At the same time the tetrabutylammonium borate eluent is converted to the low conducting boric acid. Both types of post-column reactions greatly increase the sensitivity of detection by conductivity. The conductivity detection method with the help of SPR also makes it possible to employ gradient separation are preferably carried out on silica based reversed-phase columns, rather than on polymeric based reversed-phase columns. The later type of columns shows better tolerance to increased levels of the organic solvents as well as higher separation efficiency.

Filename : [8-HPLC]
Title : HIGH- PERFORMANCE LIQUID CHROMATOGRAPHIC SEPARATION AND SELECTIVE DETECTION OF ANIONIC SURFACTANTS
APLICATION TO COMMERCIAL FORMULATION AND WATER SAMPLES

Author(s) : F. Smedes, J.C. Kraak, C.F. Werkhoven-Goewie, U.A.Th. Brinkman, R.W. Frei
Publication : Journal of Chromatography, 274 (1982), 123-132.
Summary : Reversed-phase liquid chromatography combined with post-column ion-pair extraction detection was investigated for the analysis of C10-C18 homologues of sulphonate and sulphate type surfactants. The separation were carried out on Hypersil SAS and Hypersil

ODS as the packing and water-acetone mixtures as the mobile phase. For the separation of more than five successive homologues, an acetone gradient was applied.

Anionic surfactants were detected as ion pairs by mixing of the effluent with chloroform and a solution of acridinium chloride. The ion pairs formed between the anionic solutes and acridinium ion were extracted into the chloroform phase. After phase separation the chloroform phase was monitored flourimetrically. The detection system behaved linearly for up to 4 μg of anionic surfactant injected. The detection limit ranged between 1 and 5 ng, independent of the alkyl chain length of solutes investigated. The suitability of the method for the analysis of commercial surfactant formulations and the determination of anionic surfactants at parts per billion levels in water samples, after on line on column pre-concentration, is demonstrated.

Appendix 2. Literature search Plasticizers.

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Tributyl O-acetylcitrate	1-GC	GC	Injection of standard solutions.	DB-5 capillary column; 30 m x 0.23 mm	100°C (5), rate 15°C/min, 300°C (10)	MS
Tributyl O-acetylcitrate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Tributyl O-acetylcitrate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Tributyl O-acetylcitrate	4-GC	GC	Extraction from plastic with ethyl ether or other solvents in a Soxhlet's apparatus.	V2A-Pipe (10% Resoflex LAC-2R-446) on KG 0.2-0.3 mm; 50 cm x 3 mm	230°C	FID
Tributyl O-acetylcitrate	5-GC	GC	PVC dissolved in THF by refluxing on a water bath.	Bore Pyrex glass (3.8% Silicone gum rubber OV-1 on Diatomite CQ 80/100 mesh); 1.5 m x 4 mm	100°C, rate 8°C/min, 300°C	FID
Tributyl O-acetylcitrate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (75 + 25) at a solvent rate of 2 ml/min and Methanol + water + butanol (90 + 10 + 1) at a solvent rate of 2 ml/min.	V4A-steel, Nucleosil® 50-5 200 mm x 4 mm; 6 mm and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		RI
Tributyl citrate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Tributyl citrate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Tributyl citrate	4-GC	GC	Extraction from plastic with ethyl ether or other solvents in a Soxhlet's apparatus.	V2A-Pipe (10% Resoflex LAC-2R-446) on KG; 0.2-0.3 mm;50 cm x 3 mm or V2A-Pippe (5% silicone rubber GE-30 on chromosorb); 1.20 m x 4 mm	230°C 140°C, rate 15°C/min, 400°C	FID
Triethyl O acetylcitrate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Triethyl O-acetylcitrate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Triethyl citrate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Triethyl citrate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Tris(2-ethylhexyl) O-acetylcitrate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Tris(2-ethylhexyl) O-acetylcitrate	4-GC	GC	Extraction from plastic with ethyl ether or other solvents in a Soxhlet's apparatus	V2A-Pippe (5% silicone rubber GE-30 on chromosorb); 1.20 m x 4 mm	140°C , rate 15°C/min, 400°C	FID
Tris (2-ethylhexyl) citrate	----------	----------	----------	----------	----------	----------
Bis(2-butoxyethyl) sebacate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Bis(2-ethylhexyl) sebacate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Bis(2-ethylhexyl) sebacate	4-GC	GC	Extraction from plastic with ethyl ether or other solvents in a Soxhlet's apparatus.	V2A-Pippe (5% silicone rubber GE-30 on chromosorb); 1.20 m x 4 mm	140°C , rate 15°C/min, 400°C	FID

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Bis(2-ethylhexyl) sebacate	5-GC	GC	PVC dissolved in THF by refluxing on a water bath.	Bore Pyrex glass (3.8% Silicone gum rubber OV-1 on Diatomite CQ 80/100 mesh); 1.5 m x 4 mm	100°C, rate 8°C/min, 300°C	FID
Bis(2-ethylhexyl) sebacate	6-GC	GC	Plasticizers were dissolved in THF and injected into GC.	Two stainless steel columns (10% UCW-98 on 60-80 mesh Diatoport S); each 6 ft x 1/8 in	100°C (4), rate 8°C/min, 330°C (8)	FID
Bis(2-ethylhexyl) sebacate	7-GC	GC	Injection of standard solutions.	Spiral glass column (Chromosorb Q on 100-120 mesh, impregnated with a 1% of QF-1); 8 ft x 1.8 mm	260°C/ or 160°C, rate 3°C/min, 250°C	FID
Dioctyl sebacate	1-GC	GC	Injection of standard solutions.	DB-5 capillary column; 30 m x 0.23 mm	100°C (5), rate 15°C/min, 300°C (10)	MS
Dioctyl sebacate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Dioctyl sebacate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Dioctyl sebacate	7-GC	GC	Injection of standard solutions.	Spiral glass column (Chromosorb Q on 100-120 mesh, impregnated with a 1% of QF-1); 8 ft x 1.8 mm	260°C/ or 160°C, rate 3°C/min, 250°C	FID
Dioctyl sebacate	8-GC	GC	Extraction with diethyl ether.	11 G20 Golay-coloumn (silicone rubber)	300°C	FID
Dioctyl sebacate	9-GC	GC	Solution of PVC + acetone and carbon-disulfid/ or PVC + methanol	Stainless steel column SE 30 (1.5% Chomosorb Q 60-80 mesh); 2 m x 3 mm/ and OV 17 (2.5% Chromosorb Q 60-80 mesh); 2 m x 3 mm	100°C, rate 10°C/min, 300°C	FID
Dioctyl sebacate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow of 1.8 ml/min.	„RP-18" steel column; 2 x 25 cm x 4,6 mm; 10µm		RI; UV (280 nm)

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Trialkyl(C7-C9) trimellitate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (90 + 10) at a solvent rate of 2 ml/min and Methanol at a solvent rate of 2 ml/min.	V4A-steel, Nucleosil® 50-5 200 mm x 4 mm; 6mm/ and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		UV (261 nm)
Trialkyl(C7-C9) trimellitate	3-HPLC	HPLC	Injection of standard solutions. Mobile phase: Methanol	Nukleosil 7; 250 mm x 4 mm ; C18 cartridge system with precolumn Nukleosil 7 C18; 30 mm x 4 mm		UV/VIS
Triisooctyl trimellitate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (90 + 10) at a solvent rate of 2 ml/min and Methanol at a solvent rate of 2 ml/min.	V4A-steel, Nucleosil® 50-5; 200 mm x 4 mm; 6 mm and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		UV (261 nm)
Triisooctyltrimellitate	3-HPLC	HPLC	Injection of standard solutions. Mobile phase: Methanol.	Nukleosil 7; 250 mm x 4 mm; C18 cartridge system with precolumn Nukleosil 7 C18; 30 mm x 4 mm		UV/VIS
Trioctyl trimellitate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (90 + 10) at a solvent rate of 2 ml/min and Methanol at a solvent rate of 2 ml/min.	V4A-steel, Nucleosil® 50-5; 200 mm x 4 mm; 6 mm and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		UV (261 nm)
Trioctyl trimellitate	3-HPLC	HPLC	Injection of standard solutions. Mobile phase: Methanol.	Nukleosil 7; 250 mm x 4 mm; C18 cartridge system with precolumn Nukleosil 7; C18 30 mm x 4 mm		UV/VIS

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Bis[2-(2-butoxy-ethoxy)ethyl] adipate	10-GC	GC	Injection of standard solutions.	5% polyphenyl-methyl siloxane bonded capillary column; 30 m x 0.25 mm; 0.5 μm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Bis(2-butoxyethyl) adipate	10-GC	GC	Injection of standard solutions.	5% polyphenyl-methyl siloxane bonded capillary column; 30 m x 0.25 mm; 0.5 μm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Bis(2-ethylhexyl) adipate	10-GC	GC	Injection of standard solutions.	5% polyphenyl-methyl siloxane bonded capillary column; 30 m x 0.25 mm; 0.5 μm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Bis(2-ethylhexyl) adipate	1-GC	GC	Injection of standard solutions.	DB-5 capillary column; 30 m x 0.23 mm	100°C (5), rate 15°C/min, 300°C (10)	MS
Bis(2-ethylhexyl) adipate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Bis(2-ethylhexyl) adipate	3-GC	GC	Extraction from Plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Bis(2-ethylhexyl) adipate	5-GC	GC	PVC dissolved in THF by refluxing on a water bath.	Bore Pyrex glass (3.8% Silicone gum rubber OV-1 on Diatomite CQ 80/100 mesh); 1.5 m x 4 mm	100°C, rate 8°C/min, 300°C	FID
Bis(2-ethylhexyl) adipate	6-GC	GC	Plasticizers were dissolved in THF and injected into GC.	Two stainless steel columns each (10% UCW-98 on 60-80 mesh Diatoport S); 6 ft. x 1/8 in	100°C (4), rate 8°C/min, 330°C (8)	FID
Bis(2-ethylhexyl) adipate	7-GC	GC	Injection of standard solutions.	Spiral glass column (Chromosorb Q on 100-120 mesh, impregnated with a 1% of QF-1); 8 ft x 1.8 mm	260°C/ or 160°C, rate 3°C/min, 250°C	FID
Bis(2-ethylhexyl) adipate	8-GC	GC	Extraction with diethyl Ether.	11 G20 Golay-column (silicone rubber)	300°C	FID
Bis(2-ethylhexyl) adipate	11-GC	GC	Extraction from plastic with ethyl ether or other solvents in a Soxhlet's apparatus.	V2A-Pipe (10% Resoflex LAC-2R-446 on KG; 50 cm x 3 mm	230°C	FID
Bis(2-ethylhexyl) adipate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow of 1.8 ml/min.	RP-18" steel column; 2 x 25 cm x 4.6 mm; 10 μm		RI; UV (280 nm)

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Dialkyl(C7-C9) adipate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: Methyl alcohol + water + butanol (90 + 10 + 1) at a solvent flow rate of 2 ml/min.	V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		RI
Didecyl adipate	10-GC	GC	Injection of standard solutions.	5% polyphenyl-methyl siloxane bonded capillary column; 30 m x 0.25 mm; 0.5 μm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Didecyl adipate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Didecyl adipate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper-pie with 3% sour and alcoholic washed Chromosorb W	200°C	FID
Didecyl adipate	7-GC	GC	Injection of standard solutions.	Spiral glass column (Chromosorb Q on 100-120 mesh, impregnated with a 1% of QF-1); 8 ft x 1.8 mm	260°C/ or 160°C, rate 3°C/min, 250°C	FID
Diisodecyl adipate	10-GC	GC	Injection of standard solutions.	5% polyphenyl-methyl siloxane bonded capillary column; 30 m x 0.25 mm; 0.5 μm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Diisodecyl adipate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID
Diisodecyl adipate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow of 1.8 ml/min.	„RP-18" steel column; 2 x 25 cm x 4.6 mm; 10 μm		RI; UV (280 nm)
Dioctyl adipate	10-GC	GC	Injection of standard solutions.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	50°C (1), rate 8°C/min, 300°C (10)	MS; FTIR
Dioctyl adipate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Dioctyl adipate	9-GC	GC	Solution of PVC + acetone and carbondisulfid/ or PVC + methanol	Stainless steel column; SE 30 (1.5% Chomosorb Q 60-80 mesh); 2 m x 3 mm and OV 17(2.5% Chromosorb Q 60-80 mesh); 2 m x 3 mm	100°C, rate 10°C/min, 300°C	FID
Dioctyl adipate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow of 1.8 ml/min.	„RP-18“ steel column; 2 x 25 cm x 4.6 mm; 10 µm		RI; UV (280 nm)
Bis(2-ethylhexyl) azelate	6-GC	GC	Plasticizers were dissolved in THF and injected into GC.	Two stainless steel columns .(10% UCW-98 on 60-80 mesh Diatoport S) each 6 ft. x 1/8 in	100°C (4), rate 8°C/min, 330°C (8)	FID
Bis(2-ethylhexyl) azelate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet’s apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Bis(2-ethylhexyl) azelate	11-GC	GC	Extraction from plastic with ethyl ether or methanol in a Soxhlet’s apparatus.	Glass column (10% Resoflex LAC-2R-446 on KG); 1m x 4 mm/ or Glass column Ultramol III (15% on KG); 1 m x 4 mm	220°C	FID
Diocty azelate	1-GC	GC	Injection of standard solutions.	DB-5 capillary column; 30 m x 0.23 mm	100°C (5), rate 15°C/min, 300°C (10)	MS
Diisooctyl azelate	12-GC	GC	Specially prepared sheeting formulations; solvent THF.	OV-25 (10% Chromosorb W , on 60-80 mesh); 7ft	260°C	FID

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Triphenyl phosphate	1-GC	GC	Injection of standard solutions.	DB-5 capillary column; 30 m x 0.23 mm	100°C (5), rate 15°C/min, 300°C (10)	MS
Triphenyl phosphate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID; PND
Triphenyl phosphate	3-GC	GC	Extraction from plastic with ethyl ether in a Soxhlet's apparatus.	Copper column (5% silicone rubber on sour and alcoholic washed Chromosorb W); 1.5 m x 3.2 mm	200°C	FID
Triphenyl phosphate	8-GC	GC	Extraction with diethyl ether.	11 G20 Golay-column (silicone rubber)	300°C	FID
Triphenyl phosphate	13-GC	GC	Extraction from plastic with ethyl ether.	Glass column (15% Ultramoll III on KG); 0.5 m x 4 mm/ or V2A-column (10% Resoflex LAC-2R-446 on KG); 50 cm x 3 mm	230°C	FID; PND
Triphenyl phosphate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (75 + 25) at a solvent flow rate of 2 ml/min, and methanol + water + butanol (82+ 18 + 1) at a solvent flow rate of 2 ml/min.	V4A-steel, Nucleosil® 50-5; 200 mm x 4 mm; 6 mm and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		UV (261 nm)

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Tritolylphosphate, Tricresylphosphate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID; PND
Tritolylphosphate, Tricresylphosphate	14-GC	GC	Extraction from Edible Oils with acetonitrile.	Stainless steel column (10% OV-101 on 60-80 mesh Chromosorb AW-DMCS); 10 ft x 1/8 in.	250°C	FID
Tritolylphosphate, Tricresylphosphate	1-HPLC	HPLC	Injection of standard solutions. Mobile phase: heptane + diisopropyl ether (75 + 25) at a solvent rate of 2 ml/min, And Methanol + water + butanol (82 + 18 + 1)	V4A-steel, Nucleosil® 50-5; 200 mm x 4 mm; 6 mm; and V4A-steel, Nucleosil® 10-C18; 250 mm x 4 mm; 6 mm		UV (261 nm)
Tritolylphosphate, Tricresylphosphate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow of 1.8 ml/min.	„RP-18“ steel column; 2 x 25 cm x 4,6 mm; 10 µm		RI; UV (280 nm)
Tri-o-tolylphosphate, tri-o-cresyl	14-GC	GC	Extraction from Edible Oils with acetonitrile.	Stainless steel column (10% OV-101 on 60-80 mesh Chromosorb AW-DMCS); 10 ft x 1/8 in.	250°C	FID
Tri-o-tolylphosphate, tri-o-cresyl	4-HPLC	HPLC	Injection of standard solutions. Mobile phase: a linear gradient of 25 to 80% acetonitrile in 2% aqueous acetic acid in a rate of 1.3 ml/min.	C18 cartridge filled with C18 bondapak		UV (254 nm)
Tri-m-tolyl phosphate, Tri-m-cresyl phosphate	15-GC	GC	Injection of commercially available „tricresyl phosphate“.	0.25 mm o.d. BP1 chemical bounded CP (tm) Sil CB phase	275°C	PID
Tri-p-tolyl phosphate, tri-p-cresyl phosphate	15-GC	GC	Injection of commercially available „tricresyl phosphate“.	0.25 mm o.d. BP1 chemical bounded CP (tm) Sil CB phase	275°C	PID

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Butyl benzoate	16-GC	GC	Self synthesized n-Alkyl-benzoates.	SE-30 (WCOT) column; 25 m x 0.33 mm and OV-351 WCOT column; 25 m x 0.32 mm	100°C, 2, 6, 10°C/min; 280°C. 100°C; 2, 6, 10°C/min; 230°C. Isothermal at 140, 160 and 180°C.	FID
Butyl benzoate	17-GC	GC	Injection of standard solutions.	SE-30 capillary column; 25 m x 0.33 mm, and OV-31 column; 25 m x 0.32 mm.	160°C	FID
Diethylene glycol dibenzoate	18-GC	GC	Injection of standard solution.	DEXSIL 300 GC	200°C (2), rate 10°C/min, 350°C (8)	FID
Diethylene glycol dibenzoate	5-HPLC	HPLC	Injection of standard solution in methanol. Mobile phase: methanol : water (70 : 30)	RT 250-4/ and Lichrosorb RP-18 (10 μm)		UV (254 nm)
Dipropylene glycol dibenzoate	18-GC	GC	Injection of standard solution.	DEXSIL 300 GC	160°C	FID
Diethylene glycol dibenzoate	5-HPLC	HPLC	Injection of standard solution in methanol. Mobile phase: methanol : water (70 : 30)	RT 250-4/ and Lichrosorb RP-18 (10 μm)		UV (254 nm)

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Alkyl(C8-C18) sulfonic acids	19-GC	GC	Injection of -SO3 (tBDMS).	DB-5 fused-silica column; 15 m x 0.25 mm; 0.25 μm	80°C (2), 10°C/min; 250°C	MS; FID
Alkyl(C8-C18) sulfonic acids	6-HPLC	HPLC	A standard mixture of linear alkyl sulfonates. Mobile phase: ranged from 60:40 to 30:70 acetonitrile/water and 90:10 to 40:60 methanol/water (+ 0.01 M sodium hydrogen phosphate and either 0.01 M sodium nitrate or sodium iodid = for indirect photometric detection).	Octadecyl RP-column; 250 mm x 4.6 mm		UV (242, 252, 260 nm)
Alkyl (C8-C18) sulfonic acids	7-HPLC	HPLC	A standard mixture of linear alkyl sulfonates [methanesulfonate-(C1) to tetradecylsulfonate C14)]. Mobile phase: 85% A-15% B, A: aqueous 0.5 mM tetrabutyl-ammonium borate (TBAB), B: 0.5 mM TBAB in acetonitrile; flow rates: 1 ml/min A + B, 0.3 ml/min Solid phase Reagent (SPR, cation exchange) diluted to 50 mequiv./l.	Novapak C18		Conduc-tivity; UV (214 nm)
Alkyl (C8-C18) sulfonic acids	8-HPLC	HPLC	Injection of a mixture of C_8-C_{18} alkylsulphonates. Mobile phase: gradient from water-acetone (6:4) + 0.05 M NaH_2PO4 to water-acetone (4:6), in 20 min with a linear gradient. Acridinium chloride as ion pair.	Hypersil SAS		Florimeter

Component(s)	File name	Method	Sample preparation/injection mobile phase	Column	Temperature program	Detector
Bis(2-ethylhexyl) terephthalate	2-HPLC	HPLC	Injection of standard solutions. Mobile phase: methanol: water 95:5 (v:v) at a solvent flow rate of 1.8 ml/min.	„RP-18“ steel column; 2 x 25 cm x 4,6 mm; 10µm		RI; UV (280 nm)
Bis(2-ethylhexyl) isophthalate	2-GC	GC	Injection of standard solutions.	OV-1 glass column (3% Chromosorb W HP (80-100 mesh); 4 m x 3 mm/ or SE-30 glass column (3% Chromosorb G HP (80-100 mesh); 1.5 m x 4 mm	unknown	FID