

# Trace analysis

Reagents for sample preparation,  
analysis and calibration

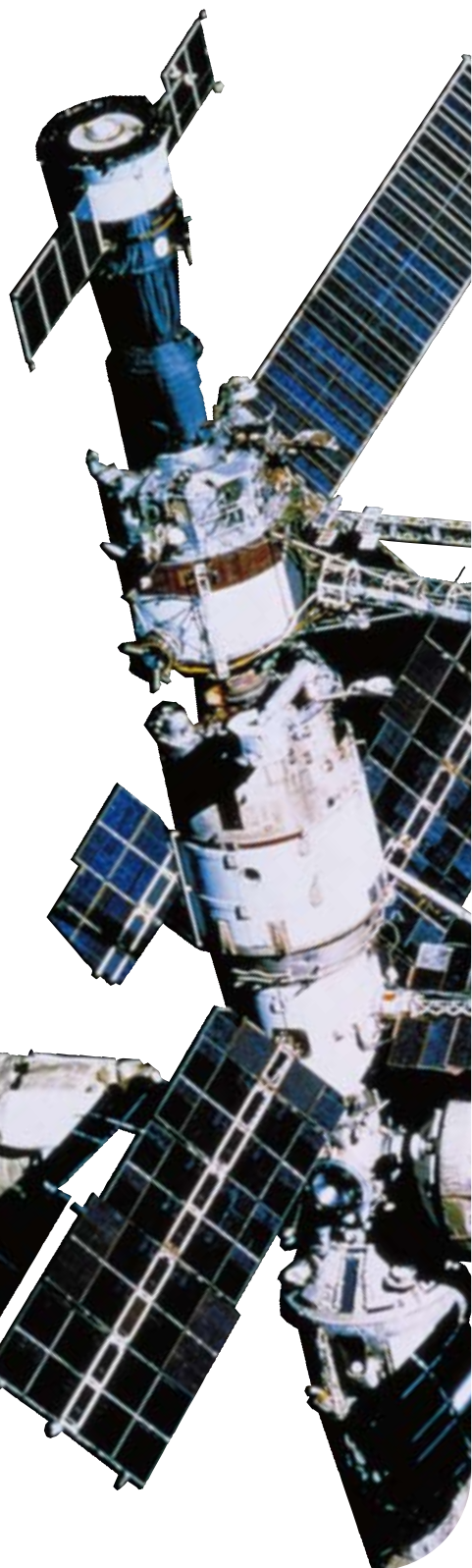
# Trace analysis

## *Reagents for sample preparation, analysis and calibration*

An analytical procedure comprises not only the physical method of determination but also several, sometimes highly complex individual steps. Only rarely can a sample be analyzed directly, i. e. without suitable pretreatment. The sample material must first be dissolved or fused.

Signals obtained must be analyzed and converted into concentrations, a process for which precisely defined reference standards are required. In order to minimise interaction of the matrix with the elements being tested for, it should be ensured that the standard largely matches the sample in terms of its physical and chemical properties.

The more sensitive the instrumental detection becomes, the more important it is to use highly pure reagents. System errors caused by impurities in the auxiliary reagents are difficult to quantify. Merck has a specially tailored range of standards and reagents to satisfy all purity requirements.



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## Sample preparation

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As a rule, trace analysis requires the sample to be available as a homogeneous solution. This is normally carried out by digestion with mineral acid, but sometimes by melting with subsequent dissolution in a mineral acid.

Digestion with acid is usually preferred; on the one hand, modern digestion technology, e.g. pressure digestion, has become a very refined technique and on the other, acids can today be produced in a higher purity than their corresponding salts.

However, X-ray-fluorescence analysis is one technique where melting digestion still plays a very important role.

## Reagents for wet digestion

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In planning an analysis, it is important to know the blank values of the reagents required.

In trace analysis in the ng/g range, Suprapur® reagents have been used for many years. Their blank values are for the most part within the range 0.1 and 2 ppb, depending on the element involved. A certificate of analysis provided with the package gives information on the batch values after filling.

For ultra-trace analysis, < 20 ppt, Ultrapur® grade acids are normally used. These acids, produced by sub-boiling distillation, are provided exclusively in bottles made of the fluoropolymer PFA. Their blank values are in the ppq range.



## Reagents for wet digestion

Designation	Quantity	Order No.
Hydrochloric acid 30% Ultrapur®	250 ml	1.01514.0250
	500 ml	1.01514.0500
	1 l	1.01514.1000
Hydrofluoric acid 48% Ultrapur®	1 kg	1.01513.1001
Hydrogen peroxide 31% Ultrapur®	1 kg	1.06097.1001
Nitric acid 60% Ultrapur®	250 ml	1.01518.0250
	500 ml	1.01518.0500
	1 l	1.01518.1000
Sulphuric acid 96% Ultrapur®	250 ml	1.01516.0250
Water Ultrapur®	1 l	1.01262.1000
Acetic acid 96% Suprapur®	250 ml	1.00066.0250
	1 l	1.00066.1000
Ammonia solution 25% Suprapur®	250 ml	1.05428.0250
	1 l	1.05428.1000
Formic acid 98–100% Suprapur®	1 l	1.11670.1000
Hydrobromic acid 47% Suprapur®	250 ml	1.00306.0250
	1 l	1.00306.1000
Hydrochloric acid 30% Suprapur®	250 ml	1.00318.0250
	1 l	1.00318.1000
Hydrofluoric acid 40% Suprapur®	500 ml	1.00335.0500
	2,5 l	1.00335.2500
Hydrogen peroxide 30% Suprapur®	250 ml	1.07298.0250
	1 l	1.07298.1000
Nitric acid 65% Suprapur®	250 ml	1.00441.0250
	1 l	1.00441.1000
ortho-Phosphoric acid 85% Suprapur®	250 ml	1.00552.0250
	1 l	1.00552.1000
Oxalic acid dihydrate Suprapur®	100 g	1.00489.0100
Perchloric acid 70% Suprapur®	250 ml	1.00517.0250
	1 l	1.00517.1000
Sodium hydroxide solution 30% Suprapur®	250 ml	1.05589.0250
	1 l	1.05589.1000
Sulphuric acid 96% Suprapur®	250 ml	1.00714.0250
	1 l	1.00714.1000



## Wet digestion of biological material

Organic digestion agents are sometimes used for biological materials. The most common is Triton® X-100, an alkylaryl polyether alcohol.

### Reagents for wet digestion of biological material

Designation	Quantity	Order No.
Dimethylsulphoxide GR	500 ml	1.02931.0500
Triton® X-100 GR	1 l	1.08603.1000

*Two principal techniques are used  
for sample preparation in  
X-ray fluorescence analysis (XRF):  
making a flux or pressing the sample into tablet form.*

## Fluxing

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Fluxing digestion is always necessary if a high degree of precision is required. Spectromelt® borates can be used for this procedure; ores, sludges, ground samples, rock, metals, alloys, ceramics and cement can be brought into homogeneous form using this technique. Interelement effects can be reduced by diluting the sample with the flux or by mixing in absorbing materials like lanthanum oxide. Spectromelt® fusing agents for XRF are characterised by high purity and bulk density, and produce stable tablets with smooth surfaces.

European standard EN 725-1 (1997) lists a mixture of lithium carbonate and boric acid (2:5) as an alternative to lithium borate for the melting digestion of aluminium oxides. If very low traces are to be analysed, this method is recommended combined with the use of Suprapur® salts.

## Grinding

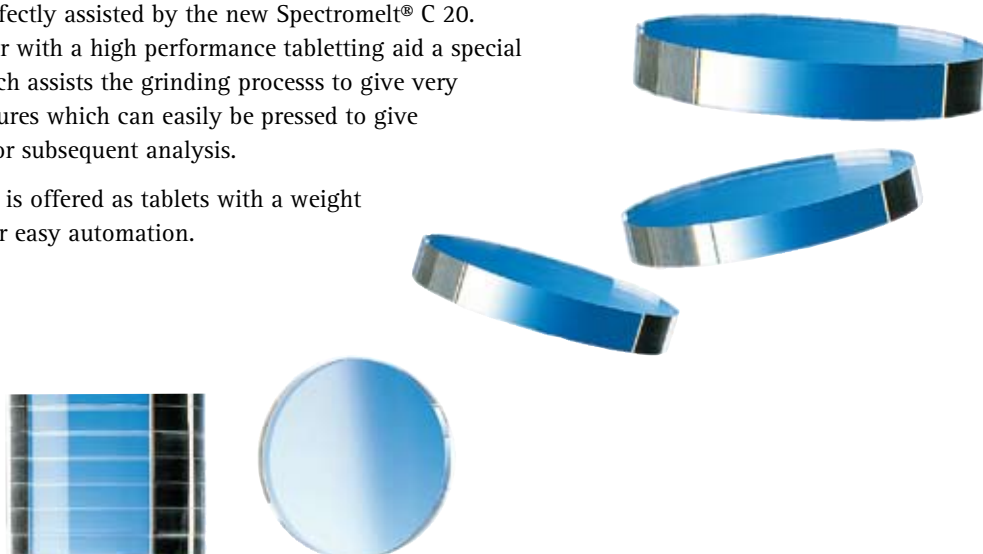
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If a finely powdered sample is to be analysed, tableting is an alternative to melting digestion. However, stable pellets cannot always be prepared without the help of a tableting agent. Hoechst Wax C micro-powder, a product produced on a large scale for use in the lacquer industry, has proved useful in this respect over many years. Suitability of the wax for the XRF analysis has been checked by performing an application test and analysis on trace impurities.

In automated sample preparation of powdered samples, speed of analysis is most important. For this purpose the sample preparation is made by grinding the sample together with a grinding and tableting aid in a high performance grinder.

This process is perfectly assisted by the new Spectromelt® C 20. It includes together with a high performance tableting aid a special cellulose type which assists the grinding process to give very homogenous mixtures which can easily be pressed to give optimum tablets for subsequent analysis.

Spectromelt® C 20 is offered as tablets with a weight of 333 mg each for easy automation.



## Fluxes for XRF

Designation		Quantity	Order No.
Spectromelt® A 10	di-lithium tetraborate	1 kg	1.10783.1000
		5 kg	1.10783.5000
		25 kg	1.10783.9025
Spectromelt® A 12	66% di-lithium tetraborate 34% lithium metaborate	1 kg	1.11802.1000
Spectromelt® A 14	51% di-lithium tetraborate 27% lithium metaborate 12% lanthanum (III) oxide 10% lithium fluoride	1 kg	1.11724.1000
Spectromelt® A 15	di-lithium tetraborate 0.4% potassium iodide	5 kg	1.24002.5000
Spectromelt® A 20	lithium metaborate	1 kg	1.12996.1000
Spectromelt® A 22	22 parts lithium metaborate 12 parts di-lithium tetraborate	1 kg	1.24001.1000
Spectromelt® A 100	di-lithium tetraborate (fused)	100 g	1.12630.0100
		1 kg	1.12630.1000
Spectromelt® A 1000	di-lithium tetraborate with 0.07% lithium bromide	1 kg	1.13175.1000
		5 kg	1.13175.5000
Spectromelt® B 10	di-sodium tetraborate	1 kg	1.06304.1000
		5 kg	1.06304.5000
		50 kg	1.06304.9050
Lithium carbonate Suprapur®		50 g	1.05676.0050
		250 g	1.05676.0250
di-Sodium tetraborate Suprapur®		25 g	1.06309.0025
		250 g	1.06309.0250
Boric acid Suprapur®		50 g	1.00765.0050
		500 g	1.00765.0500
Hoechst Wax C micro-powder		1 kg	1.09014.1000
Spectromelt® C 10	grinding and tableting aid; tablet weight: 333 mg	5 kg	1.13990.5000
Spectromelt® C 20	grinding and tableting aid; tablet weight: 333 mg	5 kg	1.13934.5000

## Melting digesting agents

Designation		Quantity	Order No.
Potassium carbonate-1,5-hydrate Suprapur®		500 g	1.04926.0500
Potassium chlorate GR		500 g	1.04944.0500
Potassium sulphate GR		1 kg	1.05107.1000
Potassium hydrogen sulphate GR Suprapur®		100 g	1.04887.0100
Sodium carbonate anhydrous Suprapur®		500 g	1.06395.0500
Sodium peroxide		500 g	1.06563.0500
		1 kg	1.06563.1000

## Application notes for Spectromelt® – Fluxing

Spectromelt® type	Recommended for digestion of
A 10, A 100, A 1000	<b>Basic oxides</b> carbonates, ground samples, magnesite, aluminium silicates, bauxite, rare earth oxides, cement, sludges, phosphates. Use of Spectromelt® A 1000 with added lithium bromide enables better separation of the melt from the digestion vessel. Spectromelt® A 100 is characterised by a particularly high bulk density of 100 g/100 ml.
A 12	Borax, cement, sludges, sand, chromium ores.
A 14	Application analogue to Spectromelt® A 12; lanthanum oxide acts as an absorbing agent. The addition of lithium fluoride lowers the melting point and reduces adherence of the melt to the digestion vessel.
A 15	Potassium iodide as anti wetting agent to increase the surface tension of the melt - easier removal out of the crucible.
A 20, A 22	<b>Acidic oxides</b> silicates, sand, clay, spinelles.
B 10	Iron, iron-, chromium-, tin- and titanium ores, rare earth minerals.

## Application notes for Spectromelt® – Grinding

Spectromelt® type	Recommended for digestion of
C 10, C 20	Ores, slags; in steel and cement analysis.



## Sample enrichment with ion exchangers

Through the use of ion exchangers, trace elements can be adsorptively bound to a solid carrier and subsequently desorbed, and hence enriched, with relatively small volumes of solvent. For trace analysis, ion exchangers of purity grade »GR« are recommended; these have been repeatedly purified and regenerated to be ready for use.

### Ion exchangers

Type	Designation	Ion form	Package size	Order No.
strongly acidic cation exchanger	Ion exchanger I	H+	500 g	1.04765.0500
	Amberlite IR-120	H+	500 ml	1.15131.0500
	Dowex 50 WX 8	H+	250 ml	1.05221.0250
	Dowex 50 WX 4	H+	250 ml	1.05238.0250
weakly acidic cation exchanger	Ion exchanger IV	H+	500 g	1.04835.0500
	Amberlite CG-50 I	H+	250 g	1.15627.0250
strongly basic anion exchanger	Ion exchanger III	OH-	500 g	1.04767.0500
	Amberlite IRA-402	Cl-	500 ml	1.12463.0500
	Amberlite IRA-410	Cl-	500 ml	1.15262.0500
	Dowex 1-X8	Cl-	250 ml	1.05242.0250
weakly basic anion exchanger	Amberlite IRA-67	OH-	500 g	1.15959.0500
	Amberlyst A 21	OH-	500 ml	1.15261.0500
mixed-bed ion exchanger	Ion exchanger V	H+/OH-	500 g	1.04836.0500
	Amberlite MB-3	H+/OH-	500 ml	1.15127.0500
	Amberlite IRN-150	H+/OH-	500 ml	1.15965.0500

## Calibration standards

The full range of calibration standards is enclosed in our brochure »Certipur®«.

Method:	Certified primary reference material:	Certified secondary reference material:	Secondary reference material:	Reference material:	Traceability:
Atomic absorption spectroscopy	–	ICP single element standards	ICP multi element standards	–	Element standards (standard reference material from NIST)
	–	–	–	AAS standards (solutions and concentrates)	Volumetric and element standards (standard reference material from NIST)
pH measurement	–	Standard reference buffer solutions and substances	–	–	Buffers (primary reference material: PTB; NIST)
	–	–	–	Buffers (Solutions and concentrates)	Buffers (primary reference material: PTB; NIST)
Conductivity measurement	–	Conductivity standards	–	–	Conductivity standards (primary reference material: PTB; NIST)
Ion chromatography	–	–	Ion chromatography standards	Ion chromatography standards	Volumetric and ion chromatography standards (standard reference material from NIST)
UV/VIS spectroscopy	–	–	UV/VIS standards	–	UV/VIS standards (standard reference material from NIST, physical methods)
Volumetry	–	–	Volumetric standards	–	Volumetric standards (standard reference material from NIST)
Additional methods	Barium sulphate white standard (certified by PTB)	–	Refractive index standards DSC standards	TOC standard, Reference colour solutions acc. Ph. Eur., 2-Propanol standard	–
HPLC	–	–	–	LiChroTest standards	–

## Auxiliary reagents for AAS – Matrix modifiers

In graphite furnace AAS, element determinations are being carried out more and more with matrix modifiers. Depending on the element to be determined, various substances are used; however, palladium nitrate has crystallised as one of the most popular.

A primary criterion for such substances is the absence of the element to be analysed. For this reason, the recommended reagents indicated below have been specially tested for their suitability as matrix modifiers.

### Matrix modifiers

Designation	Quantity	Order No.
Magnesium matrix modifier $c(\text{Mg}) = 10.0 \pm 0.2 \text{ g/l}$ [ $\text{Mg}(\text{NO}_3)_2$ in 15% $\text{HNO}_3$ ]	50 ml	1.05813.0050
Palladium matrix modifier $c(\text{Pd}) = 10.0 \pm 0.2 \text{ g/l}$ [ $\text{Pd}(\text{NO}_3)_2$ in 15% $\text{HNO}_3$ ]	50 ml	1.07289.0050
Phosphate matrix modifier $c(\text{NH}_4\text{H}_2\text{PO}_4) = 100 \pm 0.2 \text{ g/l}$ [ $\text{NH}_4\text{H}_2\text{PO}_4$ in water]	50 ml	1.07290.0050
Ammonium dihydrogen phosphate Suprapur®, suitable as matrix modifier	50 g	1.01440.0050
L-(+)-Ascorbic acid GR	100 g	1.00127.0100

## Determination of mercury

A number of procedures can be used for the determination of mercury by AAS. The most common of these is the reduction method using tin (II) chloride, for which numerous reagents low in mercury content are available. However, the hydride process is also frequently used.

The sodium borohydride available, apart from its low blank values for the hydride-forming elements like arsenic or antimony, also has a low mercury content.

### Determination of mercury

Designation	Quantity	Order No.
Sodium borohydride GR	100 g	1.06371.0100
Hydroxylammonium chloride (max. 0.000 001% Hg)	250 g	1.04619.0250
Potassium chromate (max. 0.000 001% Hg)	500 g	1.04865.0500
Potassium permanganate (max. 0.000 005% Hg)	1 kg	1.05084.1000
Perchloric acid 70% (max. 0.000 000 5% Hg)	1 l	1.00514.1000
Nitric acid 65% (max. 0.005 ppm Hg)	2.5 l	1.00452.2500
Sulphuric acid 95–97% (max. 0.005 ppm Hg)	2.5 l	1.00732.2500
Tin (II) chloride dihydrate (max. 0.000 001% Hg)	250 g	1.07814.0250

## Spectroscopic buffers for flame AAS

In flame AAS, spectroscopic buffers are often used to suppress physical, ionisation and chemical interferences. The Schuhknecht and Schinkel buffer solution as used in the determination of alkali elements has become particularly important. A multi-element standard for the elements lithium, sodium and potassium is also available for this method.

The Schinkel buffer solution enables the method to be expanded to include up to 14 mono and divalent elements, simple calibration being all that is required for the analysis.

### Spectroscopic buffers for flame AAS

Designation	Quantity	Order No.
Caesium chloride-aluminium nitrate buffer solution according to Schuhknecht and Schinkel (contains 50 g/l CsCl and 250 g/l Al(NO <sub>3</sub> ) <sub>3</sub> )	1 l	1.02037.1000
Caesium chloride-lanthanum chloride buffer solution according to Schinkel (contains 100 g/l La and 10 g/l CsCl)	1 l	1.16755.1000

## Reagents for electrochemistry

In addition to the solutions available for filling electrodes, the range includes two TISAB (= total ionic strength adjustment buffer) solutions for use with fluoride electrodes.

### Reagents for electrochemistry

Designation	Quantity	Order No.
Potassium chloride solution 3 mol/l	250 ml	1.04817.0250
Potassium chloride solution 3 mol/l saturated with silver chloride	100 ml	1.04818.0100
TISAB solution, ready-for-use	500 ml	1.15368.0500
TISAB III solution, ready-for-use	500 ml	1.16770.0500

### Application notes for Spectromelt® – Grinding

	TISAB		TISAB III	
Calibration	Fluoride standard solution	50 ml	Fluoride standard solution	90 ml
	TISAB solution	50 ml	TISAB III solution	10 ml
Analysis	sample	50 ml	sample	90 ml
	TISAB solution	50 ml	TISAB III solution	10 ml



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