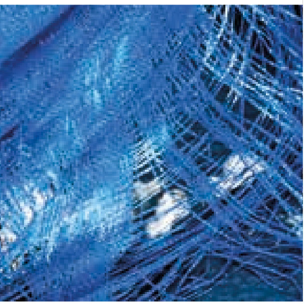
Polymer and plastics analysis



Quality control for polymer production

Metrohm

Metrohm ...

- is the global market leader in titration
- offers a complete portfolio for NIR and Raman analysis, in addition to all of the methods of ion analysis, titration, electrochemistry (e.g. voltammetry), and ion chromatography
- is a Swiss company and manufactures exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for anion chromatography
- provides you with unparalleled application expertise
- offers you more than **2000 applications** free of charge
- supports you with dependable on-site service worldwide
- is not listed on the stock exchange, but is owned by a foundation
- takes a sustainable approach to corporate management, putting the interests of customers and employees ahead of maximizing profit

Content

Metrohm – customized polymer analysis for quality control of monomers, intermediate products, and finished polymers

Polymers and plastics are a mainstay of modern life due to their versatility and physical properties: they can be formed into nearly any shape, with different degrees of flexibility and other variable parameters. They have to meet supreme standards.

Plastic components are widespread; they are used in airplanes and cars, packaging, medical devices and products, electronics, and countless other products. Every year 370 million tons of plastic are produced worldwide.

Polymers also have a dark side: plastic waste is growing all the time. Plasticizers are harmful to human health. Halogens in plastic create corrosive and toxic hydrogen-halides during combustion. Finally, there is the issue of microplastics infiltrating every corner of the environment.

Polymer production is a demanding process in which high-purity raw materials undergo complex reactions and are turned into polymers, fibers, resins, rubbers, and gums. To ensure that these products meet stringent specifications, raw materials and processes must be monitored along the entire production chain. Analyses must be carried out at every stage of production. It's a complex process. Also, some finished polymer products become feedstock for other goods and enter as raw materials in various industries such as: paper, cosmetics, textile, or the building material industry. That makes the production process even more tricky.

Metrohm offers about 100 applications to help control the process of polymer production from monomer analysis through to final control of finished products. Techniques range from titration and ion chromatography to spectroscopy and voltammetry.

You can count on our know-how

Metrohm offers you complete solutions for very specific analytical issues. Your Metrohm contacts are professionals, who develop customized applications and provide you with professional support in all matters concerning polymer analysis. We offer standardized methods and secondary methods like Raman and NIR from one provider. Our know-how, our experience, and our optimized methods help to increase throughput in a time-saving and accurate way with lower cost.

In this brochure, we present some selected applications used during polymer production. Do not hesitate to contact our application specialists for help and more information.

Application Note (AN): Throughout the brochure the abbreviation «AN» stands for Application Note. You can find all the mentioned ANs in the Application Finder on our homepage www.metrohm.com/applications/

1. Analytical techniques

1.1. Titration

Potentiometric titration is ideally suited for titrating functional groups in monomers, in particular monomeric mono- and polyacids as well as polyols. These titrations are mostly carried out in nonaqueous, nonpolar solutions and are thus accompanied by very little potential change, leading to flat and erratic titration curves. Metrohm has overcome these drawbacks by developing instruments and sensors (e.g., Solvotrode easyClean) that allow equivalence points to be determined in low-conductivity media. Hundreds of titrations are applied in the polymer industry: from **acid, hydroxyl, epoxy, carboxyl, and amine number to chloride and isocyanate content.** The most common and readily automated analyses are **hydroxyl and acid number** as well as isocyanate content. Their titrimetric determination is mainly regulated by ASTM and ISO standards.

1.2. Karl Fischer titration

You can check the **water content** in gaseous and liquid monomers, in liquefied gases as well as in solid monomers in raw materials and even in finished plastics using Karl Fischer titration. Sensitive coulometric Karl Fischer titration is the ideal method for determining water content at trace levels. As most polymers are not soluble, water determination is carried out using the **Karl Fischer oven method,** where residual moisture in the plastic is evaporated and transfered to the titration cell where it is subsequently titrated.

1.3. Ion chromatography

Ion chromatography (IC) and combustion ion chromatography have become efficient and precise methods to quantify compounds in the production of polymers, from raw materials to finished consumer goods to components in effluent streams. New technologies such as ultrafiltration, automatic multipoint calibration and specialized cation analysis help monitor effluent streams more easily and accurately than ever. This ensures that the concentration of byproducts from polymer manufacturing processes meet regulated limits. Ion chromatography may also be used for other analyses, such as anions in perfluorocarbon material (AN-S-228), anions in PVC (AN-S-130), sodium, ammonium, and potassium in polyethers (AN-C-059), and phosphate and sulfate in polymer samples after inline dilution & inline dialysis (AN-S-230).

In polyols, alkali metals represent some of the most **critical impurities,** because they are strong catalysts for linear and branched reactions. Ion chromatography after inline matrix elimination is a rapid and precise method for the simultaneous determination of sodium and potassium. Additionally, IC is an effective technology for **final production testing** and environmental monitoring applications in the polymer industry.

1.4. Combustion ion chromatography

Combustion Ion Chromatography (CIC) is well-suited for analyzing halogens, sulfur, and polychlorinated biphenyls (PCBs) in raw materials and finished products. Driven by recent technical advances in **automation,** CIC has improved both its accuracy and ease of use. Standard IC is routinely used for the measurement of various anions and cations in discharge water for NPDES (National Pollutant Discharge Elimination System) compliance, and for quantification of amines in raw material and effluent monitoring. In this inline technique, the sample undergoes pyrohydrolytic combustion, where the compounds of interest are converted into gaseous form and then directly absorbed by a solution. This solution is then analyzed via ion chromatography.

Combustion Ion Chromatography is an invaluable tool for the analysis of both raw materials and finished components in the polymer industry.

1.5. PVC-Thermomat method

Metrohm's 895 Professional PVC Thermomat determines the **thermostability of polyvinyl chloride (PVC) and other chlorine-containing polymers** by means of the dehydrochlorination test (DHC). This involves exposing the samples to elevated temperatures in the PVC Thermomat and measuring the stability time – the time until gaseous hydrogen chloride is released. The method is compliant with national and international standards, and it is particularly easy to perform.

1.6. Near-Infrared Spectroscopy (NIRS)

Metrohm laboratory analyzers for near-infrared (NIR) spectroscopy enable users to perform routine analysis (e.g., determination of hydroxyl number of polyols) quickly and reliably – without requiring sample preparation or additional reagents and yielding results in less than a minute. These analyzers are capable of performing qualitative and quantitative analysis of a number of physical and chemical parameters in one run.

Vis-NIR spectroscopy is highly suited to analyze various polymers such as polyurethanes, PET, PVC, nylon etc. Common parameters determined by Vis-NIR spectroscopy are hydroxyl number, density, viscosity, melt flow index, acid number, moisture content, diethylene glycol, and carboxylic end groups, to name but a few. As measurements by Vis-NIR spectroscopy only take a few seconds, it is the preferred method for real-time monitoring of chemical reactions. Looking beyond chemical parameters, Vis-NIR spectroscopy is also used to determine blending homogeneity or particle size distribution. The combination of real-time analysis with superior accuracy and reliability makes Vis-NIR spectroscopy a matchless technique for the polymer analysis.

1.7. Raman spectroscopy

With our handheld Raman analyzers, you can identify common monomers comfortably and rapidly. Monomers such as styrene, various alkyl methacrylates, divinylbenzene, ethylene glycol, phenol, terephthalic acid, and urea can be analyzed within seconds. Moreover, additives or inhibitors such as benzoquinone can be identified quickly and unambiguously. Metrohm Instant Raman Analyzers (Mira) combine ease of use with maximum safety and provide results within seconds. Raman can effectively distinguish materials such as ABS, PE, PS, PET, and PMMA* in waste, irrespective of color, surface water, deformation, or dirt.

*Acrylonitrile-butadiene-styrene copolymers (ABS), polyethylene (PE), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA)

1.8. Voltammetry

Voltammetry is a very sensitive technique for the analysis of electrochemically active substances, such as inorganic or organic ions and can also analyze neutral organic compounds. Voltammetry is very well suited to analysis of raw material quality in polymer manufacturing. This technique combines a wide range of applications, short analysis times, and high precision and sensitivity with comparatively low investment and operation costs.

1.9. Electrochemistry

Our electrochemistry portfolio ranges from portable instruments to modular systems for full flexibility and multichannel workstations allowing a number of experiments to be performed simultaneously. Electrochemical measurements are used for the characterization of electrochemically active materials and interfaces which involve electron or charge transfer (e.g., conductive polymers). Electrochemical measurements are all based on a highly accurate control and measurements of voltage, current, electrical charge, or impedance and are realized with specially designed potentiostats/galvanostats. Research encompasses the progressive development trajectory of the compounds from theory and concept validation of new materials to characterization and quality control of materials and devices. One of the hottest materials currently being studied is **graphene**. Graphene is apt for electrochemical research because it has special electrical, optical, and mechanical properties and is a two-dimensional covalently linked polymer. It is used extensively as electrode material and substrates in many electrochemistry application fields. Specially modified, ready-to-use graphene screen-printed electrodes (SPE) are available from Metrohm DropSens. Essential measurement techniques in the NOVA 2 software, used with any of the potentiostats/galvanostats provided by Metrohm Autolab, allow in-depth research in this field.

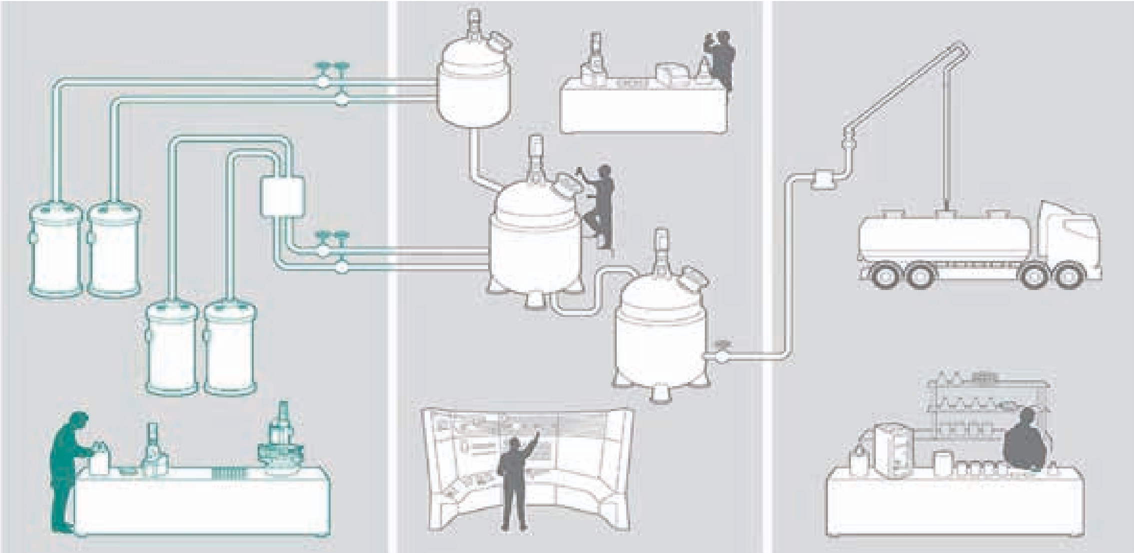
1.10. Multimethod process analysis

Our inline, online, and atline process analyzers allow you to monitor different parameters in real time, continuously, and fully automatically. They can thus be seamlessly integrated into almost any production process. Our industrial process analyzers are available for a wide range of analytes and in various configurations – ranging from single-parameter systems to multiparameter analyzers performing titration, ion chromatography, voltammetry, photometry as well as direct measurements or measurements with ion-selective electrodes.



2. Applications

2.1. Quality control for raw materials



A final product can only be as good as the materials used to make it. Regular and systematic analyses of incoming starting material assure certain identity and quality attributes of the final product before the production process has begun. Given the importance of raw material quality, analyses must be specific, reliable, and precise – and given the importance of economic aspects such as time to market, analyses must be efficient and time-saving as well.

Metrohm offers a range of instruments and methods that meet any requirements in raw materials inspection: from easy-to-use out-of-the-box systems to customized setups tailored to your application challenge. In addition, Metrohm gives you access to an extensive pool of industry-specific application know-how free of charge.

Parameter	Standard	Matrix	Method
Acid number	ASTM D4662	Polyol (in PU production)	Titration
Acidity	ASTM D5629 ASTM D6099 ISO 14898	Low-acidity aromatic isocyanates and PU prepolymers Moderate- to high-acidity aromatic isocyanates Aromatic isocyanates in PU production	Titration
Free acidity	EN ISO 1061	Unplasticized cellulose acetate	Titration
Alkalinity/basicity	ASTM D4662 ASTM D6979 ISO 14899 ASTM D6437	Polyol (in PU production)	Titration
Total aldehydes	ASTM D7704	Styrene monomer	Titration
Total chlorine	ASTM D4661	Isocyanates	Titration
Hydrolyzable chlorine	ASTM D4663	Isocyanates	Titration
Degree of unsaturation	ISO 17710 ASTM D4671	Polyol (in PU production)	Titration
Hydroxyl groups	ASTM E1899	Polyol (in PU production)	Titration
Hydroxyl number	ASTM D4274 ISO 14900 ASTM D6342 ISO 15063	Polyol (in PU production)	Titration NIRS NIRS
Permanganate absorption number	ISO 8660	Caprolactam	Photometry
Water	ASTM D5460 ASTM D4672 ISO 14897	Rubber additives Polyol (in PU production) Polyol (in PU production)	KFT KFT

2.1.1. Water determination

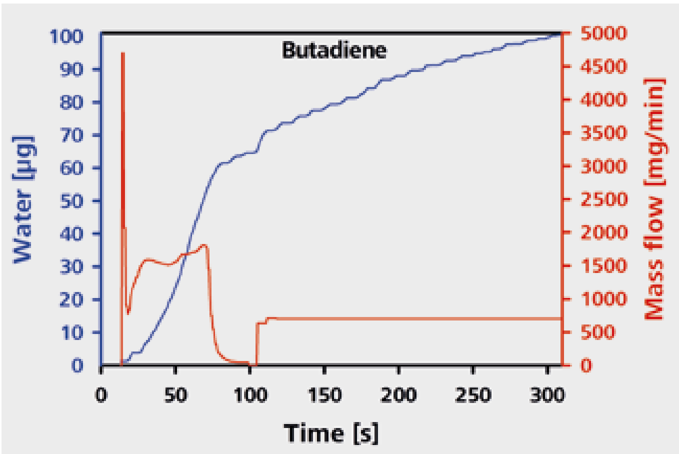
Contaminants in raw materials like water can significantly hamper the production process. Water can be quantified using Karl Fischer titration regardless of the physical state of the monomer. You can check the water content in gaseous and liquid monomers as well as in liquefied gases using Karl Fischer titration. Additionally you can analyze solid samples with the KF oven method.

874 USB Oven Sample Processor, 851 Titrando (coulometric cell) and titration software ***tiamo***.

Water determination in liquid monomers

APPLICATION NOTES:

- Water in melamine **AN-K-034**
- Water in beta-caprolactam **AN-K-035**



Butadiene gas – water determination

Water determination in gaseous monomers

APPLICATION NOTES:

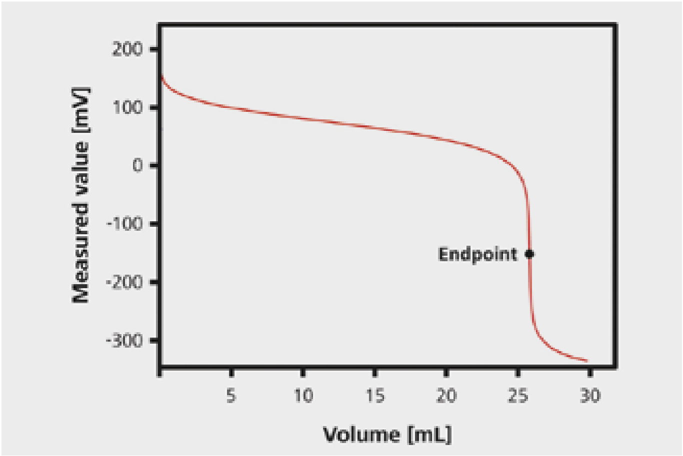
- Water in propene **AN-K-066**
- Water in butadiene **AN-K-060**

855 Robotic Titrosampler for acid/base titration

2.1.2. Acid number, hydroxyl number, isocyanate determination

When acrylic acid dimerizes, the acid groups of two monomers react with one another. The number of free acid functions per gram of material thus reflects the dimer content. The acid number – i.e., the amount of potassium hydroxide (KOH) in milligrams which is required to neutralize one gram of sample – is therefore determined as a quality indicator. This is done by **titration** (figure below).

The titration takes place in a nonaqueous solution. The low conductivity of the medium makes it harder to determine the endpoint potentiometrically, but suitable sensors such as the Metrohm Solvotrode easyClean enable precise determinations nonetheless. The analysis can be fully automated.



Acid number as per ASTM D4662 and ISO 2114.

Determination of acid number

APPLICATION NOTES:

- Acid value, hydroxyl value, and isocyanates in raw materials for plastics by titration **AB-200**
- Partial acid number in unsaturated polyester resin in accordance with EN ISO 2114 **AN-T-164**
- Total acid number in unsaturated polyester resin according to EN ISO 2114 **AN-T-165**
- Acid number in acrylic acid **AN-T-160**

Hydroxyl number as per ASTM E1899, EN ISO 4629-2, and EN ISO 2554

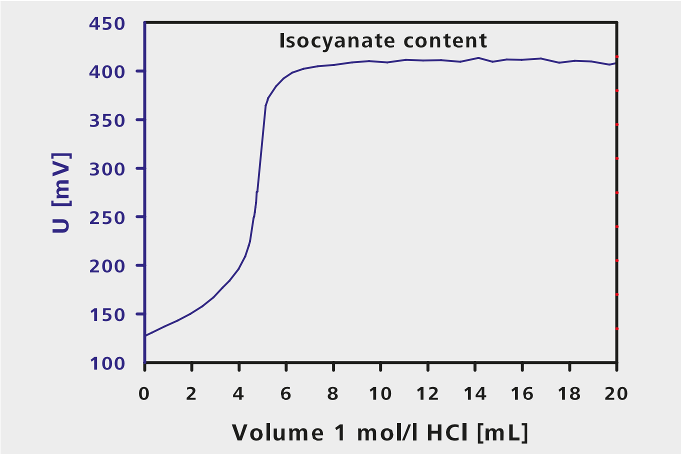
APPLICATION NOTES:

- Fully automated potentiometric determination of the hydroxyl number (HN) according to ASTM E1899 and EN ISO 4629-2 **AB-322**
- Hydroxyl number in polyols and oxo alcohols according ASTM E1899 **AN-T-178**
- Hydroxyl number in polyols and oxo alcohols according to EN ISO 4629-2 **AN-T-177**

Isocyanates as per EN ISO 11909, EN ISO 14896, and EN ISO 2554

APPLICATION NOTES:

- Isocyanate in unsaturated polyester resin and polyurethane resin in accordance with ISO 14896 **AN-T-167**
- Acid value, hydroxyl value, and isocyanates in raw material for plastics by titration **AB-200**



Isocyanate determination

Feedstock analysis/parameter check in real time by spectroscopy

APPLICATION NOTES:

- Hydroxyl in polyols **AN-NIR-006**
- Isocyanate content using Vis-NIR spectroscopy **AN-NIR-068**
- Hydroxyl number in liquid polyols using Vis-NIR spectroscopy **AN-NIR-035**
- Simultaneous determination of multiple quality parameters of polyols using Vis-NIRS **AN-NIR-065**

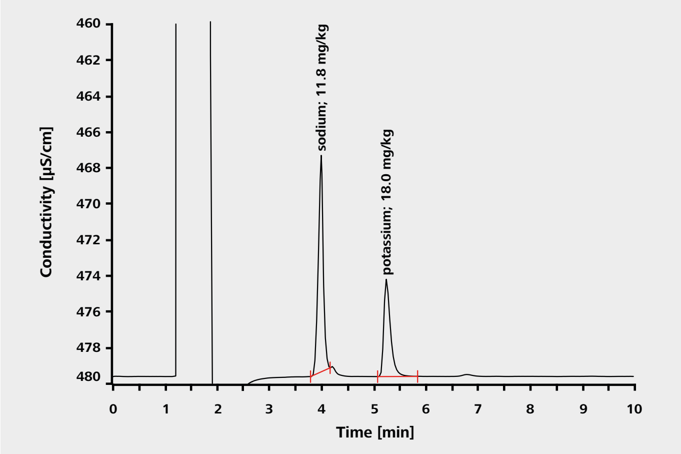
2.1.3. Impurities

Sodium and potassium in polyol by IC

There are also contaminants in raw materials, like sodium and potassium, that can significantly impair the production process.

APPLICATION NOTE:

- Sodium and potassium in polyol using IC following inline matrix elimination **AN-C-157**



Sodium and potassium determination

4-CBA in polyterephthalic acid and iron in ethylene glycol

APPLICATION NOTES:

- Polarographic determination of 4-carboxybenzaldehyde in terephthalic acid by polarography **AB-190**
- 4-Carboxybenzaldehyde in polytherephthalic acid **AN-V-062**
- Iron (total) in ethylene glycol with 2,3 dihydroxynaphthalene **AN-V-123**

884 Professional VA semiautomated, single determination.

2.1.4. Inhibitors: Online process analysis for raw material testing

TBC in styrene, butadiene, or vinylacetate

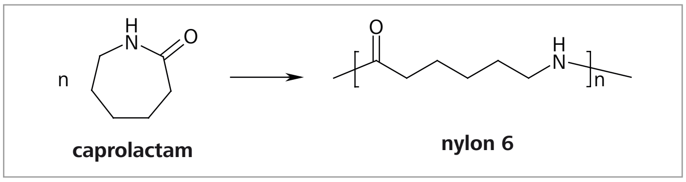
APPLICATION NOTE:

- 4-tert-butylcatechol in styrene in accordance with ASTM D4590 **AN-PAN-1027**

Caprolactam purity monitoring in accordance with ISO 8660

APPLICATION NOTE:

- Permanganate absorption number **AN-PAN-1011**

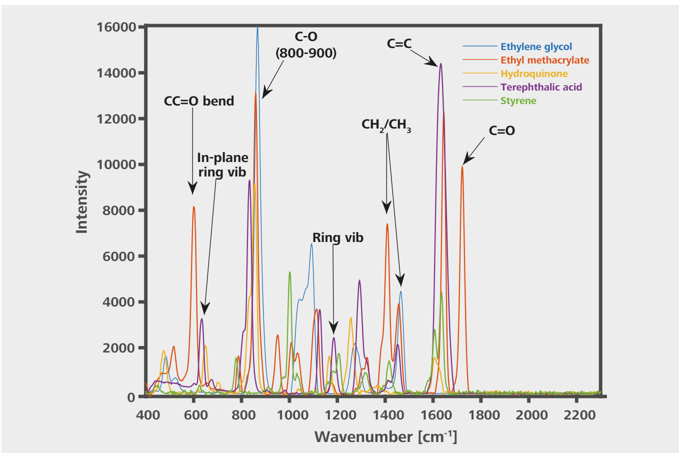


Carbolactam determination

2.1.5. Identification of raw materials using Raman spectroscopy

How does it work? The instrument illuminates a sample with laser light and then detects scattered photons. Elastically scattered photons have the same energy before and after interacting with the sample, so they do not provide any information about the identity of the sample. They are of no value for determination. In the case of in-elastically scattered photons, interactions between light and the sample result in changes in the frequency of photons. This change in frequency provides information about the sample: these shifts are characteristic of the molecular structure of the sample. The resulting pattern – the Raman spectrum – of each substance is unique, providing an unambiguous fingerprint for each molecule. The figure below shows the Raman spectra of some common monomers.

Peak positions in the Raman spectra provide information about the molecular structure of a sample molecule. The difference between the frequency of incident and scattered photons, the Raman shift, corresponds to characteristic bond vibrations, which can be used to identify a molecule. Chemometric analysis and library matching allow for assignment of each spectrum to a known compound.



Raman spectra of some common monomers.

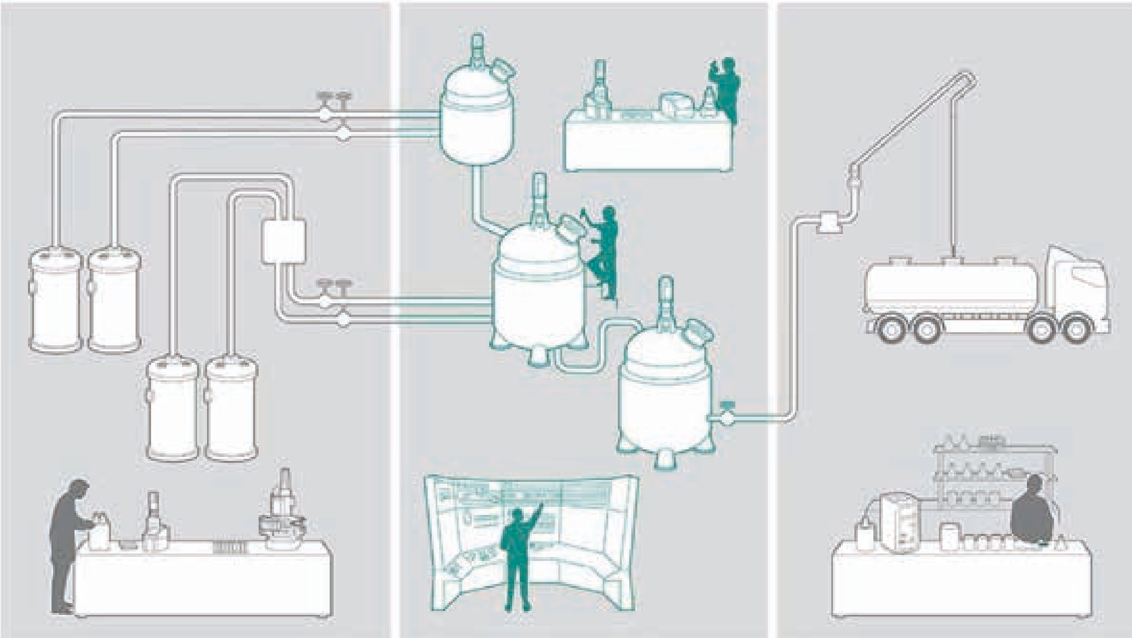
Monomers determination

APPLICATION NOTE:

- Identification of monomers with Raman **AN-RS-008**

This Application demonstrates the convenient identification of conventional monomers within seconds using the handheld Mira analyzer. Monomers such as styrene, various alkyl methacrylates, divinylbenzene, ethylene glycol, phenol, terephthalic acid, and urea can be distinguished. Additives or inhibitors such as benzoquinone can be identified quickly and unambiguously.

2.2. Intermediates/reaction monitoring



With NIRSystems, you can benefit from technologies that provide tailored solutions that make your industrial processes safer, more eco-friendly, and more effective.

Spectroscopic methods are predestined for polymerization process monitoring. Available as benchtop, as well as inline monitoring systems, Metrohm NIRSystems analyzers help you track what is going on in your reactors. These techniques yield results in seconds, do not require any chemical reagents, and are nondestructive. With these systems, you no longer have to worry about sampling or sample preparation.

Process optimization through real-time analyses with spectroscopy

APPLICATION NOTES:

- Analysis of polymer using near-infrared spectroscopy **AB-414**
- Inline monitoring of free isocyanate content in polyurethane **AN-PAN-1041**
- Near-infrared analysis of polyols: process monitoring in rough environments **AN-NIR-007**

Reaction monitoring using online and inline process analyzers

More than four million tons of viscose fibers are produced worldwide each year for the textile industry. Viscose is produced from cellulose, a natural polymer which is obtained from pulp. The fibers are produced using the wet-spinning method in a bath containing sulfuric acid, sodium sulfate, and zinc sulfate. Each of these substances has a different task in the production process. Altering their concentrations changes the properties of the fibers, enabling different types of viscose fibers to be produced.

Online determination of acid and zinc concentrations is essential for controlled production. It can be carried out simultaneously with the ADI 2045TI Process Analyzer from Metrohm Process Analytics. The ADI 2045TI Ex proof Process Analyzer is the preferred solution for hazardous environments where explosion proof protection is a must. Our NIRS XDS Process Analyzer provides up to nine inline measuring channels helping to monitor several process streams simultaneously without chemical reagents.

Sulfuric acid and zinc sulfate in viscose/rayon production

APPLICATION NOTE:

- Sulfuric acid and zinc sulfate **AN-PAN-1010**

Determining sulfuric acid traces in acetone and phenol

APPLICATION NOTE:

- Sulfuric acid in acetone and phenol **AN-PAN-1008**

Analysis of dyeing plastics during manufacturing

APPLICATION NOTE:

- Identification of various polymer master batches with Raman Spectroscopy **AN-RS-007**

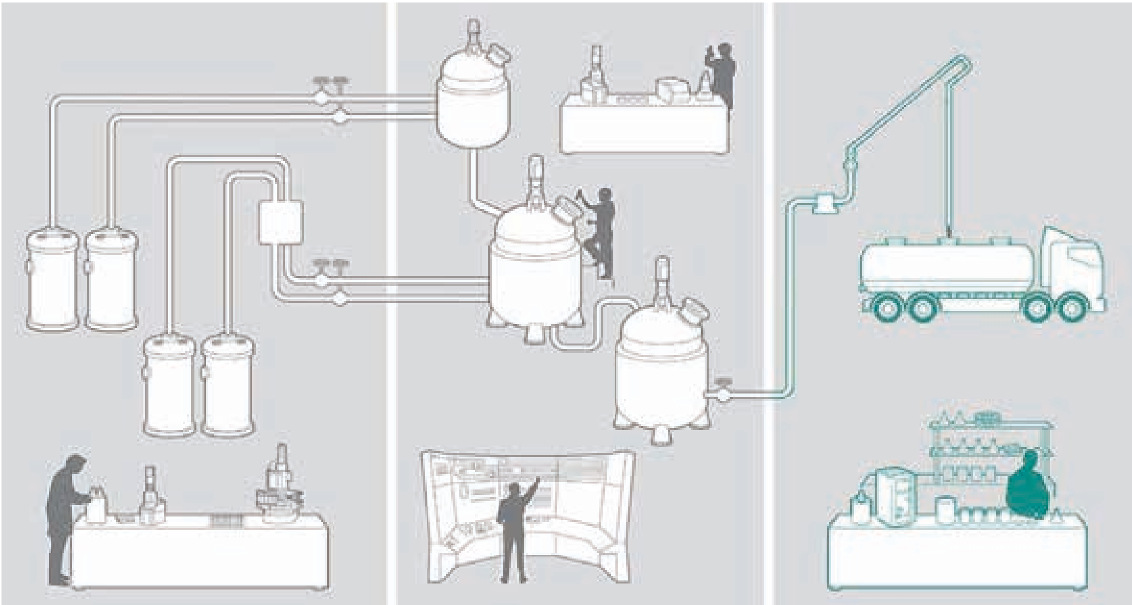
Solvent monitoring/recovery

In many chemical processes, solvents can be a significant cost incurred in producing the final polymer product. A way to optimize production costs for polymers is to look at improving solvent recovery processes. Solvent recovery systems help reduce consumption of pure solvent, save on waste disposal, and reduce liability associated with storing excess on-site. Ensuring that recovered solvents are sufficiently pure for their intended reuse or are safe for disposal is made simple with analytical techniques that determine halogen, sulfur, water and methanol levels.

APPLICATION NOTES:

- Monitoring the purity of recovered solvents with NIRS, **AN-NIR-021**
- Halogens and sulfur in residual solvent using Combustion IC, **AN-CIC-002**

2.3. Quality control of the finished polymer



High-performance polymers are used in virtually any industry and are essential components of many consumer products. The carefully designed properties of every polymer are achieved through very precise and complex production steps. To ensure that the polymers conform to specifications, quality control of the finished products is a key aspect in the production chain.

Standards for quality control in polymer and plastics production

Parameter	Standard	Matrix	Method
pH value	EN ISO 1264 ISO 8975	Vinyl chloride resins Plastic, phenolic resins	pH value
Electrical conductivity	ISO 9944	Plastics, phenolic resins	Conductivity
(Total) Acid number	ASTM D1386 EN ISO 2114	Synthetic and natural waxes Polyester resins, paints and varnishes (binders)	Titration
Amine groups	ISO 9702	Amine epoxide hardeners	Titration
Epoxy contents	ASTM D1652	Epoxy resins	Titration
Hydrolyzable chloride	ASTM D1726	(Liquid) Epoxy resins	Titration
Epoxide equivalent	ISO 3001	Epoxide compounds	Titration
Free phenols	ISO 119	Phenol-formaldehyde mouldings	Titration
Hydroxyl groups	ASTM E1899	Polyol (in PU production)	Titration
Hydroxyl value	EN ISO 2554 EN ISO 4629-2	Unsaturated polyester resins Binders for paints and varnishes	Titration
Vinyl acetate content	ISO 8985	Ethylene-vinyl acetate copolymers (EVA) and further thermoplastics (VA/AA, PVA, PVCA)	Titration
Formaldehyde content	ISO 11402	Phenolic and amino resins	Titration
Water	ASTM D6869 ISO 15512 SH/T 1770	Plastics Polyethylene (PE)	KFT
Thermostability	ISO 182-3	Vinyl chloride homo-/copolymers	Oxidation stability
Bromine	EN IEC 62321-3-2	Halogen-free cable and wires	Combustion Ion Chromatography
Carboxyl end groups	ASTM D7409	Polyamides/Polyester	Titration
Epoxy contents	ASTM D1652	Epoxy resins	Titration
Rubber	ISO 19242	Determination of total sulfur content	IC

2.3.1. Water determination

Excessive amounts of water in finished products may adversely affect their properties. Sensitive coulometric **Karl Fischer titration** is the ideal method for determining low water content. As most polymers are not water soluble, the analysis is carried out using the **Karl Fischer oven method:** the residual moisture in the plastic is heated in order to evaporate it prior to titration.

Water content in different plastic types

Polymer type	ABS[1]	PA[2]				PPA[3]	PC[4]	PET[5]		Standard	
Sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	HYDRANAL®-Water Standard KF-Oven, 220...230°C, 5.57 ± 0.05%	
Oven temperature	230°C	230°C	150°C	150°C	150°C	150°C	230°C	230°C	230°C		230 °C
1	1371.0	1078.2	1059.7	907.8	1006.3	695.7	1180.4	2196.2	1661.2	**1 & 2**	5.63 5.56
2	1382.9	1103.0	1057.0	925.0	1028.4	755.9	1167.4	2146.2	1644.3	**3 & 4**	5.52 5.54
3	1384.3	1116.2	1078.4	940.8	1042.6	741.2	1186.0	2144.1	1632.5	**5 & 6**	5.59 5.54
4	1398.1	1183.4	1120.7	993.9	1049.7	773.4	1185.9	2176.1	1635.2	**7 & 8**	5.48 5.50
5	1401.1	1199.2	1114.2	972.0	1065.7	786.6	1174.1	2203.8	1648.5	**9 & 10**	5.58 5.48
Mean value [µg/g]	**1387.5**	**1136.0**	**1086.0**	**947.9**	**1038.5**	**750.6**	**1178.8**	**2173.3**	**1644.3**		**5.54%**
Uncertainty[a] [µg/g]	**15.2**	**65.4**	**37.0**	**43.4**	**27.9**	**43.7**	**10**	**34.3**	**14.2**		**0.034%**

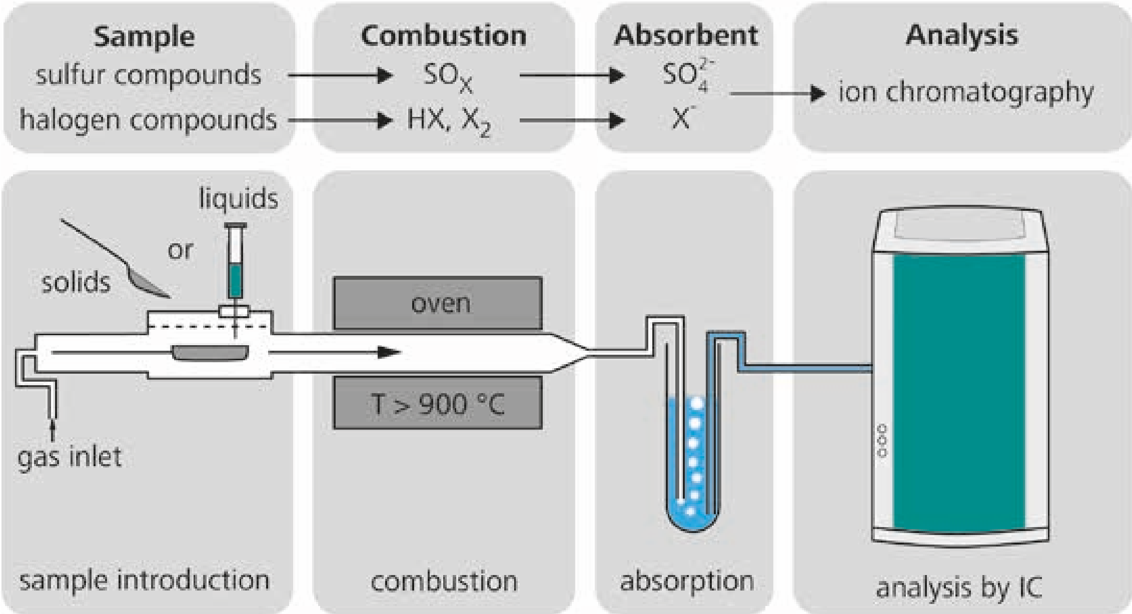
[1]ABS = acrylonitrile-butadiene-styrene-copolymer, [2]PA = polyamide, [3]PPA = poly(phthalamide), [4]PC = polycarbonate,
[5]PET: poly(ethylene terephthalate)
[a]Uncertainty = student t-factor × standard deviation × (number of single determinations)$^{0.5}$

APPLICATION NOTES:

- Water content of soft contact lenses **AN-NIR-020**
- Parallel determination of water content by KF and potentiometric acid-base titration **AN-K-068**
- Water in plastic pellets – Interference-free determination based on ASTM D6869 **AN-K-049**
- Water in expandable polystyrene – Oven system with closed sample vials simplifies analysis **AN-K-017**

2.3.2. Halogens and sulfur in polymers

The halogens present in polymer waste can potentially enter into the environment as carcinogenic compounds. This has led to efforts to reduce halogen content in components used in the manufacturing of various electronic and consumer products and materials. Regulations affecting composition, waste, and energy use in the production of polymer products have already been adopted in many countries.



Combustion IC drastically reduces the need for front-end sample preparation as the sample is pyrolyzed in an oxidizing environment. The resulting gaseous hydrogen halide is trapped in an absorption solution followed by direct analysis by IC. This is a straightforward, fully automated process which both reduces analysis time and yields reproducible results.

DIN EN 62321-3-2 stipulates CIC for determining total bromine in electric and electronic products

APPLICATION NOTE:

- Chlorine, bromine, and sulfur in low-density polyethylene applying Combustion Ion Chromatography **AN-S-290**

Compliance with Restriction of Hazardous Substances directive (RoHS) requires that the halogen content in various organic materials is drastically reduced. This has created a great demand for halogen-free polymers for various manufacturing operations. (AN-CIC-010).

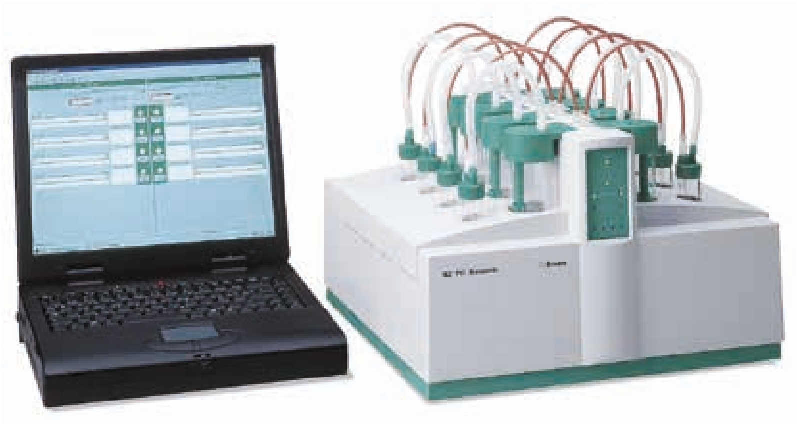
Polyisobutene (PIB) is an important raw material for the manufacturing of fuel and lubricant additives to control corrosion. Monitoring of halogens is important during the manufacturing of additives for corrosion control. PIBs are also used in the manufacturing of synthetic rubber and as a base material for the manufacture of chewing gum. (AN-CIC-008).

Determination of the following parameters with CIC:

Parameter	Matrix	Application Note
chlorine, bromine, sulfur	low-density polyethylene	AN-CIC-003
halogens, sulfur	latex gloves	AN-CIC-004
chlorine, bromine, sulfur	polyethylene pellets	AN-CIC-006
fluorine	polyisobutene	AN-CIC-008
halogens	polymers	AN-CIC-010
bromide	polystyrene	AN-CIC-022
halogen, sulfur	chlorinated and brominated halobutyl rubber	AN-CIC-021
chlorine, bromine, sulfur	low-density polyethylene	AN-S-290
chlorine, bromine, sulfate	electronic material	AN-CIC-015

Important norms and standards:

- Total bromine polymers by Combustion ion chromatography as per **IEC 62321-3-2**
- Electronic base material tested for halogen-free definition applying CIC as per **IEC 61249-2-21**
- Rubber total sulfur content with CIC as per **ISO 19242**



763 PVC Thermomat with PC.

2.3.3. Heat resistance of PVC

Dehydrochlorination test as per ISO 182-3: Measuring the thermostability of polymers

APPLICATION NOTES:

- Thermostability of PVC and other chlorine-containing polymers **AB-205**

This Application Bulletin describes the determination of the thermostability of PVC in accordance with ISO 182 Part 3 using the dehydrochlorination method with the 895 Professional PVC Thermomat. This instrument enables the fully automatic determination of the stability time. The test is suitable for monitoring the manufacturing and processing of PVC products during the injection molding process as well as during final inspection. The comparison of PVC products and testing the effectiveness of heat stabilizers are other applications of this method.

- Thermostability of pure, blended, and processed PVC **AN-R-008**
- Thermostability of PVC **AN-R-016**

2.3.4. Carboxyl determination

APPLICATION NOTE:

- Carboxyl end groups in polymers – Photometric determination based on ASTM D7409 **AN-T-087**

DS2500, Multisampler with polymer sample

2.3.5. Spectroscopy for polymer testing

Checking additives in finished plastics

APPLICATION NOTES:

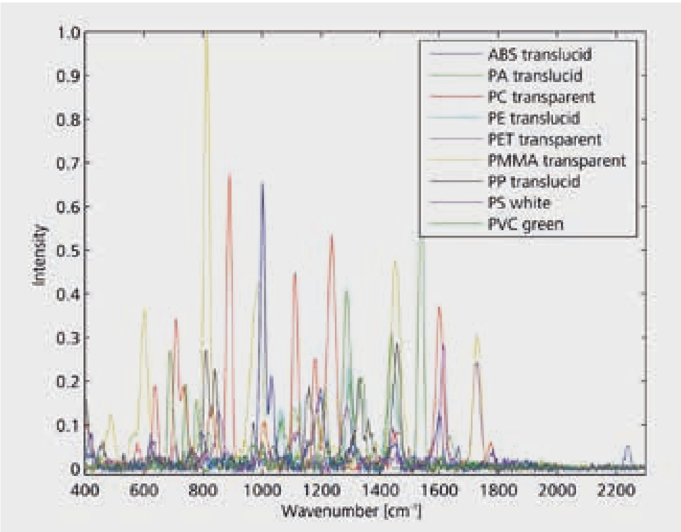
- Determination of additives in polymer pellets by near-infrared **AN-NIR-004**
- Determination of coatings on nylon fibers by near-infrared spectroscopy **AN-NIR-005**
- Diethylene glycol, isophthalic acid, intrinsic viscosity, and acid number in PET granulate by NIRS **AN-NIR-023**
- Textile analysis using near-infrared spectroscopy **AB-413**
- Determination of amine number and solid content of dipping paint **AN-NIR-030**
- Analysis of polymer granulate using near-infrared spectroscopy **AN-NIR-034**
- Quality control of polyamide using Vis-NIR spectroscopy (Nylon) **AN-NIR-060**
- Simultaneous determination of multiple quality parameters in epoxy resins using Vis-NIR spectroscopy **AN-NIR-067**

Checking copolymer levels in finished plastics

APPLICATION NOTE:

- Analysis of copolymer levels in polymer pellets by near-infrared spectroscopy **AN-NIR-003**

This application describes the determination of copolymer levels in polyethylene (PE) and polyvinylacetate (PVA) pellets using NIRS. The determination of the composition of the polymer blends takes less than 30 seconds and requires no sample preparation. The second derivative spectra are analyzed by the linear least-squares regression method.



Checking copolymer levels in finished plastics by spectroscopy.

Fast identification of postconsumer plastic with material type analysis for recycling

APPLICATION NOTE:

- Identifying Polymers with Raman Spectroscopy **AN-RS-001**

This Application Note describes the Raman spectroscopy identification of polymers such as ABS, PE, PS, PET and PMMA* in various dyes. Rapid and non-destructive determination takes place after a suitable spectrum database has been created. Measurements with the Raman spectrometer Mira require no sample preparation and provide immediate and unambiguous results.

* Acrylonitrile-butadiene-styrene copolymers (ABS), polyethylene (PE), polyethylene terephthalate (PET), polymethyl methacrylate (PMMA)

2.3.6. Residuals and impurities

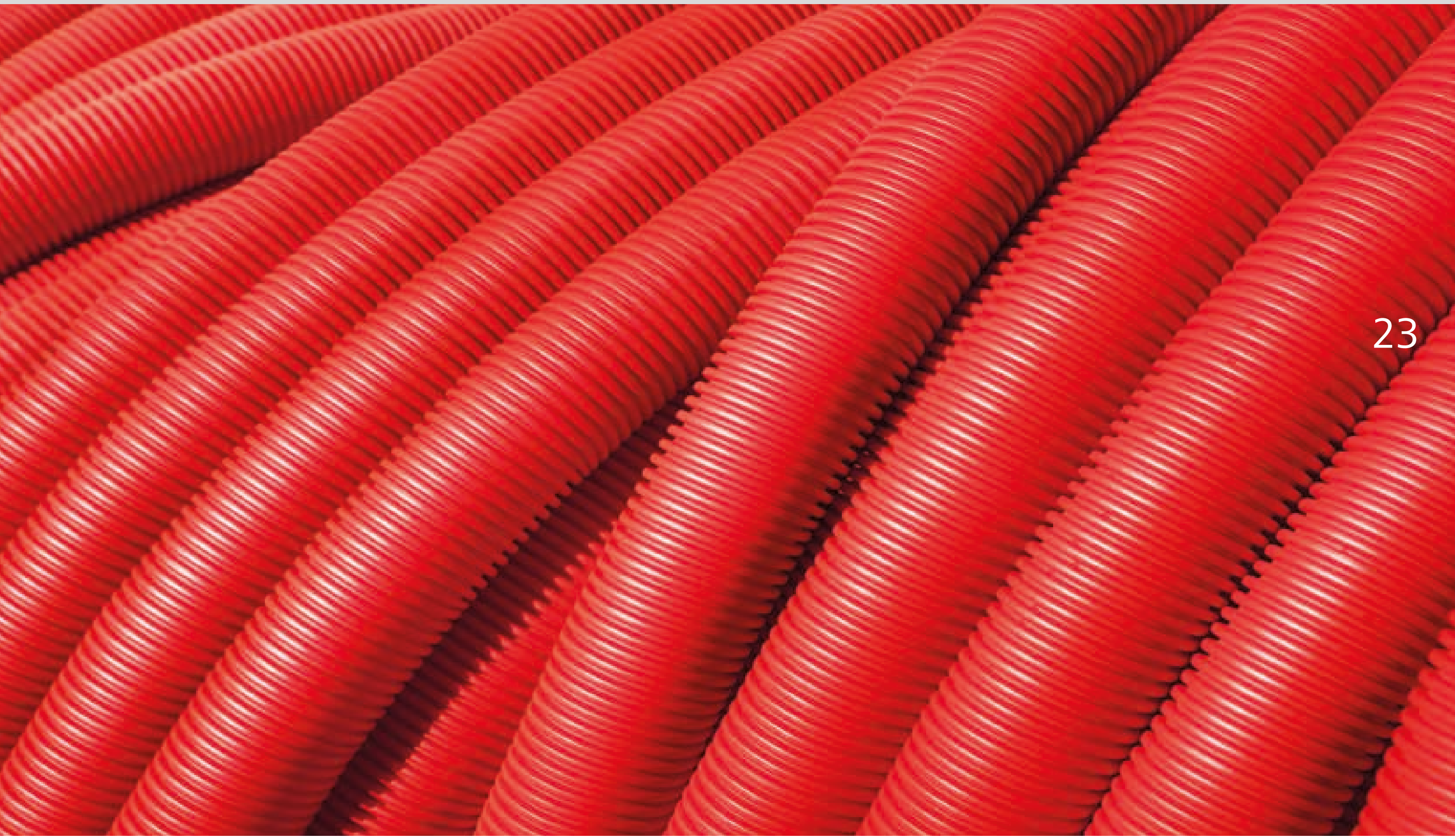
IC has proven to be an effective technology for final product testing and environmental monitoring applications in the polymer industry.

APPLICATION NOTES:

- Phosphate and phosphite in poly(vinylphosphonic acid) using dialysis for sample preparation **AN-S-063**

This AN describes the determination of phosphate and phosphite in poly(phosphonic acid) using anion chromatography with conductivity detection after chemical suppression and dialysis for sample preparation.

- Fluoride, glycolate, chloride, and oxalate in a latex dispersion **AN-S-122**
- Six anions in PVC **AN-S-130**
- Anions in perfluorocarbon **AN-S-228**



More IC applications for determination of impurities

Parameter	Matrix
melamine	acetic acid
borate	resin powder
cations	finely ground polymer
zinc	finely ground polymer
silicate	finely ground polymer
fluoride, phosphate, sulfate	concrete, cement, plasticizer
phosphate and sulfate	polymers
sodium	acrylate resin
cations	PVC
anions	PVC
formate and acrylic acid	polymer
sodium, potassium	epoxy resin
chloride, bromide, nitrate	epoxy resin
phosphate, phosphite	30% polyvinylphosphonic acid

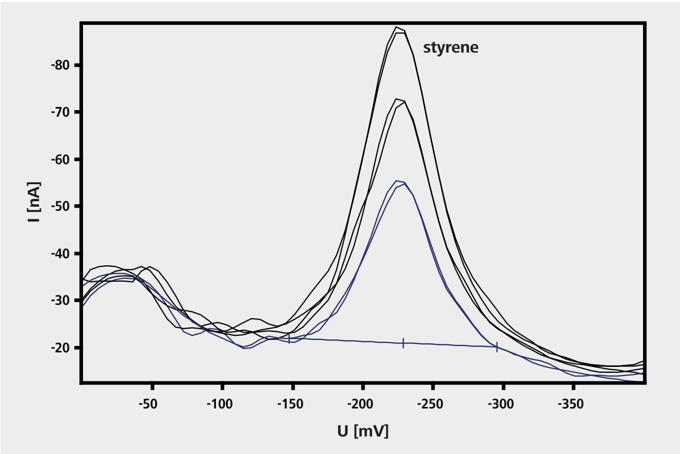
Styrene in finished polystyrene / example food packaging and toxic styrene

APPLICATION NOTES:

- Polarographic determination of styrene in polystyrene and copolymers **AB-136**

This Application Bulletin describes a simple polarographic method to determine monomeric styrene in polymers. The limit of determination lies at 5 mg/L. Before the determination, styrene is converted to the electrochemically active pseudonitrosite using sodium nitrite.

- Free styrene in polystyrene and mixed polymers **AN-V-064**



Styrene determination

Heavy metals in polymers

APPLICATION NOTES:

- Titanium in polyethylene terephthalate (PET) **AN-V-113**
- Cobalt in polyethylene terephthalate (PET) **AN-V-114**
- Antimony in polyethylene terephthalate (PET) **AN-V-115**

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2.3.7. Electrically conductive polymers

In general, synthetic polymers are isolators. However, if they possess an extensive π electron system, they can (semi)conduct electricity. The most common conducting polymer (CP) materials are polyaniline, polypyrrole, as well as polythiophene and its derivatives. By incorporating doping ions or substituents, metal-like conductivities and other exceptional properties are obtained. These materials are used from organic light-emitting diodes (OLEDs) to polymer solar cells or conducting polymer-based supercapacitor devices and electrodes. To investigate the electrochemical properties of conducting polymers or of polymer electrolytes during electrodeposition, in situ measurements such as electrochemical impedance spectroscopy (EIS) and cyclic voltammetry are required. In these leading-edge technologies, researchers all over the world rely on Metrohm Autolab instruments.

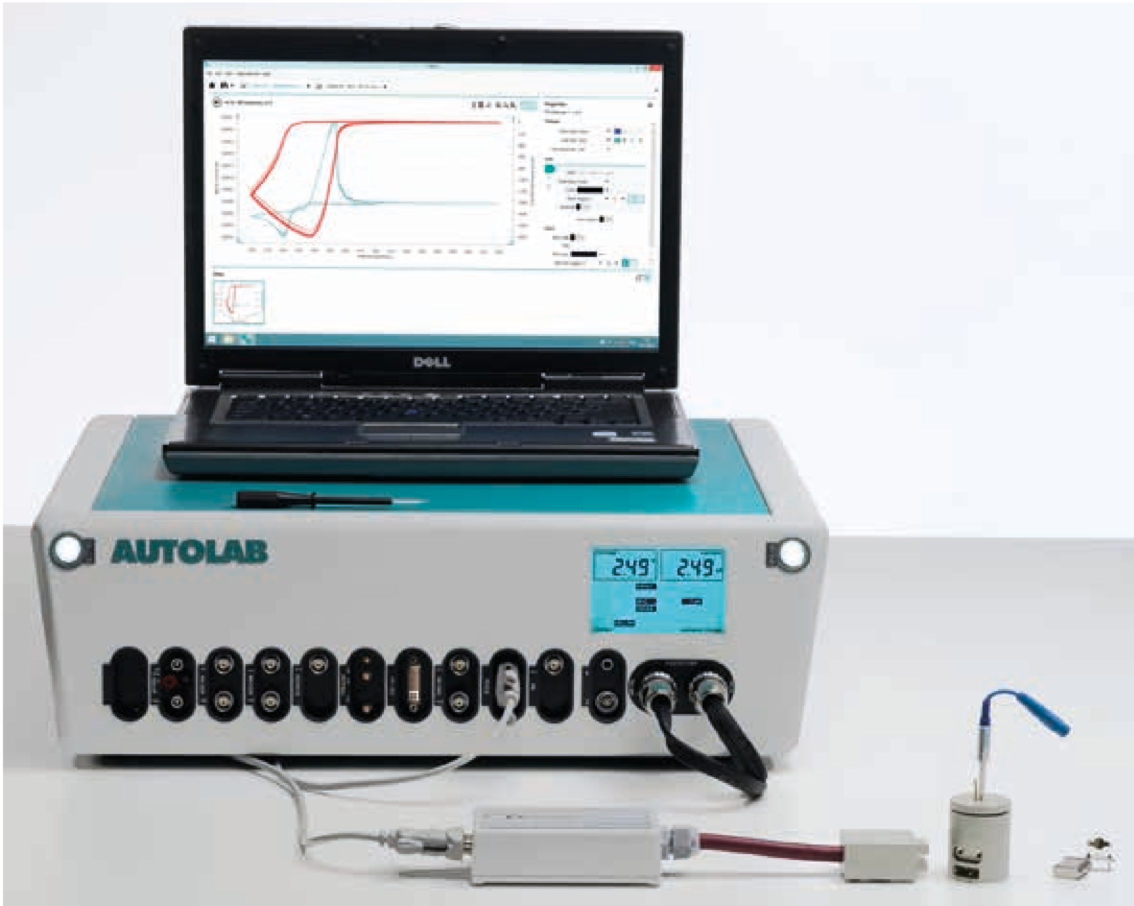
The synthesis, characterization, and use of conductive polymers play an important role within the polymer industry because of the versatile applicability of these materials in different areas such as: energy storage and generation devices, electrochromic displays, sensors, electrocatalysis, corrosion protection, and coatings.

Various electrochemical techniques can be applied to research in the field of conducting polymers: Cyclic voltammetry (CV), Chronoamperometry (CA) and Chronocoulometry (CC). These can be used in hyphenation with Quartz Crystal Microbalance (QCM) and are the most common techniques used to monitor formation and deposition of polymers as well as the kinetics of charge transfer mechanisms. Electrochemical Impedance Spectroscopy (EIS) is the most powerful electrochemical technique used for in-depth characterization of the charge transfer mechanisms and interfacial processes which may take place between the conducting polymer and the environment (electrolyte).

Other non-electrochemical techniques can also be used simultaneously with electrochemistry to further understand the nature of charge transport within materials and the relationship between the structure of a material and its chemical and electrochemical properties. Some examples of analytical techniques which can be combined with electrochemistry: UV-VIS spectroscopy, microscopy (optical, AFM, STM, SECM), and ellipsometry.

Metrohm Autolab offers a full range of electrochemical instruments and accessories to meet the needs of researchers working in the field of conductive polymers.

Parameter	Standard	Matrix
DC Resistance	ASTM D4496	Moderately Conductive Materials
Volume Resistivity	ASTM D991	rubbers used in electrically conductive and antistatic products
DC Resistance	ASTM D257	Standard Test Methods for DC Resistance or Conductance of Insulating Materials
Electrical Properties	ASTM STP926	Engineering Dielectrics Volume IIB Electrical Properties of Solid Insulating Materials: Measurement Techniques
Resistance	ISO 2878	Rubber, vulcanized -- Antistatic and conductive products -- Determination of electrical resistance



Autolab PGSTAT302N with an EQCM module with laptop and NOVA 2.

www.metrohm.com

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