Original Paper

Analytical investigation of dust, sludge and waste water specimens from the production facilities of a special glass manufacturer[1])

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Waste materials obtained at the production of special glasses need to be investigated for their constituents quickly, precisely, and sufficiently sensitivly in order that they can be recycled as raw materials to the batch, or that appropriate disposal measures can be initiated. The solid specimens from the environment, such as dust and sludge, are decomposed using mineral acids or alkali melts, while the waste waters in most of the cases are decomposed by means of HNO_3/H_2O_2. In the event of high concentrations the elements are determined by mensuration analysis, while in the case of low (< 100 mg/l) and trace (< 0.1 mg/l) concentrations, induced coupled plasma spectrometry, atomic spectrometry in absorption (flame, graphite tube, hydride, and cold-vapour atomic absorption spectrometry) and in emission, respectively, and solvent spectrophotometry are employed.

Analytische Untersuchung von Staub-, Schlamm- und Abwasserproben einer Spezialglashütte

Die bei der Produktion von Spezialgläsern anfallenden Abfallstoffe müssen schnell, genau und ausreichend empfindlich auf ihre Inhaltsstoffe untersucht werden, damit sie als Rohstoff erneut dem Gemenge zugegeben oder entsprechende Entsorgungsvorgänge eingeleitet werden können. Die festen Umweltproben wie Staub und Schlamm werden mit Mineralsäuren oder alkalischen Schmelzen, die Abwässer meist mit HNO_3/H_2O_2 aufgeschlossen. Die Elementbestimmung erfolgt bei hohen Konzentrationen mittels Maßanalyse, bei geringen Konzentrationen (< 100 mg/l) und im Spurenbereich (< 0.1 mg/l) mit der Plasmaspektrometrie, der Atomspektrometrie in Absorption (Flammen-, Graphitrohr-, Hydrid- und Kaltdampf-Atomabsorptionsspektrometrie) bzw. in Emission und der Lösungsspektralfotometrie.

1. Introduction

The separation of useful materials from the waste – mostly already at the place of origin – is of great significance at Schott Glaswerke. This is due to the growing environmental consciousness, the new laws on waste material duties, the ever larger problems associated with scarcer disposal space and, last not least, the cost-saving re-use of waste materials as a raw material.

At Schott Glaswerke some 400 glasses of different compositions and properties are melted from approximately 250 different raw material components, which means the waste to be disposed of in terms of cullet, outlet air, dust, condensate, sludge, as well as about 2.5 million m^3 of waste water is in the order of roughly 36 000 t/a [1].

Clear identification of the waste materials is of great significance both for recycling as the materials can be re-utilised only if their contents are calculable, and for disposal as all non-identifiable waste materials need to be deposited at toxic waste disposal dumps because it cannot be ruled out that compounds are included that make standard-type depositing along with non-industrial refuse impossible.

A variety of analyses methods is available for the investigation of these waste materials. Waste materials whose compositions vary to a small extent only are subjected to the x-Ray Fluorescence Analysis (RFA) in most of the cases, while waste waters and solid waste of varying compositions, e.g. dusts from outlet air purification plants, are investigated by means of wet-chemical analyses methods.

2. Description of analyses methods

2.1. Cullet

Cullet of like nature from the productions centre of the various glass tanks can in the majority of cases be re-added to the respective glass batch without any difficulty. If necessary it is analysed using the RFA method.

Classical silicate analyses methods not dealt with in detail here are employed for the investigation of non-identified cullet. The addition of the latter as a glass raw material is likely to be problematical.

2.2. Dusts

As for the dusts, the concentration of oxides of lead, calcium, strontium, sodium, potassium, chromium,

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iron, sulphur as well as fluorine and chlorine are of interest. The determinations are carried out in accordance with the analysis plan as follows:

PbO:
- fume-off and dissolution, respectively, with HNO_3,
- addition of EDTA solution of known concentration level in excess,
- adjustment of the 5.5 pH value with hexamethylenetetramine,
- complexing of impurity elements with NaF (removal of excess by means of H_3BO_3),
- back titration by means of lead nitrate solution of a known concentration level.

CaO, SrO, BaO, Na_2O, K_2O:
- decomposition with $HF/HClO_4$,
- after fume-off of fluorides,
- take-up of residue by means of HCl,
- determination of element concentration levels by means of atomic spectrometry methods (Atomic Absorption Spectrometry (AAS) / Auger Electron Spectroscopy (AES)).

Cr_2O_3, Fe_2O_3:
- fume-off with HNO_3,
- take-up of residue with HNO_3,
- determination of element concentration levels by AAS or, in cases of low concentration levels, by means of the solvent spectrophotometry.

F^-:
- decomposition by means of pyrohydrolysis after adding V_2O_5 in superheated water vapour (alternatively, water vapour distillation or Na_2CO_3/ZnO sintering decomposition may be employed; DIN 51 084 [2]). Fluoride determination may be employed, using the ionsensitive electrode. If the fluorine concentrations are high, determination may also be performed by mensuration analysis, with titration by means of $ZrOCl_2$ being employed.

Cl^-:
- dissolution of substance with HNO_3; perhaps short-duration boil-up,
- addition of excessive $AgNO_3$ solution of known concentration level,
- back titration of excessive level with NH_4SCN solution against Fe(III) sulphate.

SO_3:
- pyrolytic decomposition in the O_2 stream,
- IR spectrometric determination of SO_2.

In cases of a more complex sample matrix, alkali fusion decompositions ($Na_2O_3/Na_2B_4O_7$ or NaOH), $K_2S_2O_7$ fusion decompositions, or a combination of the two decomposition methods are used.

If further components of the contents are required to be investigated, the determination by means of plasma emission spectrometry (ICP/AES) or AAS is recommended after decomposition with $HF/HClO_4$ [3].

Table 1. Emission lines and detection limits in the determination of elements by the use of ICP/AES

element	emission lines in nm	lower limit of application range in mg/l
arsenic	189.042	0.05
	193.759	0.05
antimony	206.833	0.05
	217.581	0.05
cadmium	214.438	0.01
	226.502	0.01
	228.802	0.01
lead	220.353	0.1
chromium	205.552	0.01
	267.716	0.01
	283.563	0.01
nickel	231.604	0.02
copper	324.754	0.01
	327.396	0.01
zinc	206.191	0.01
	213.856	0.005

2.3. Waste water

A major portion of the water used is employed for cooling the glass melting process and it is not be contaminated and will be circulated, respectively. It can be piped directly into the sewerage. But the water used, for instance, for sawing, grinding, and for polishing glass, suffers contamination and has to be purified first and subsequently analysed for its harmlessness in accordance with the sewage water duties regulations before it can be fed into the sewerage [4].

To this end, the ICP/AES as well as the AAS methods with the respective techniques, such as graphite tube, hydride and cold-vapour AAS, are used. As far as the ICP/AES method is concerned, the sample solution is introduced into an argon plasma by means of a peristaltic pump, where the elements are activated by the argon plasma to emit. This multielement method offers high sample throughput, low detection limits, a large linear operating range and, in most cases, slight matrix effects. In the event of a complex matrix, it is recommended to adapt to the sample solution the predosage level matrix and that of the mostly only one reference solution, which contains all the elements to be determined with the concentration levels known.

The methods listed below are applied for the determination of concentration levels of arsenic, antimony, cadmium, lead, chromium, nickel, copper, cobalt etc. (onto 0.01 mg/l):
- decomposition with HNO_3/H_2O_2,
- take-up of residue with HNO_3,

Table 2. Results of a dust analysis

dust composition	mean value $\bar{X}$ in wt%	standard variation s	number of analyses n
PbO	64.95	0.205	10
CaO	8.55	0.138	8
SrO	0.26	0.012	6
BaO	9.50	0.197	15
Na_2O	1.31	0.042	6
K_2O	0.83	0.024	6
Cr_2O_3	0.12	0.015	6
Fe_2O_3	0.046	0.003	6
F^-	0.56	0.017	6
Cl^-	1.71	0.198	6
SO_3	3.1	0.25	6

Table 3. Analytic investigation results of a synthetic waste water

waste water composition	synthetic composition in mg/l	analysis of synthetic composition in mg/l	method of analysis
As	0.05	0.071	ICP/AES
Sb	0.10	0.11	ICP/AES
Cd	0.02	0.014	ICP/AES
Pb	0.2	0.16	ICP/AES
Cr	2.0	2.0	ICP/AES
Ni	0.2	0.18	ICP/AES
Cu	0.3	0.25	ICP/AES
Zn	0.1	0.10	ICP/AES
Mo	0.04	0.039	graphite tube AAS
Se	0.02	0.022	hydride AAS
Hg	0.001	0.0008	cold-vapour AAS
Cr^{3+}	1.5	1.4	photometry
Cr^{6+}	0.5	0.48	photometry

- performing of measurements by ICP/AES at wavelengths and concentration levels given in table 1. This method is established as a DIN standard [5].

For more sensitive measurements (< 0.01 mg/l):
- decomposition,
- concentration (e.g. carbamate complexes extracted in organic solvents),
- measurement by means of graphite tube AAS [6 and 7];

arsenic, antimony, selenium (tellurium, zinc):
- decomposition with H_2SO_4/H_2O_2 (alternatively, $MgO/MgNO_3$),
- determination by means of hydride AAS [6 and 8];

mercury:
- measurement using cold-vapour AAS [9];

$Cr^{3+/6+}$:
- addition of EDTA solution,
- at the same time, determination of Cr^{3+} ions (blue complex with EDTA) and self-colouration of Cr^{6+} ions at various wavelengths by means of solvent spectrophotometry [10].

2.4. Sludges and condensates

The aforementioned decomposition and determination methods, optimised for the special matrices, are also used for analytically determining sludges and condensates of which only minor quantities are obtained [11].

3. Results and discussion

Applying the methods of section 2., a dust analysis (table 2) was carried out and a synthetically produced waste water was analysed. The analysis values are evident from the nominal/actual value comparison of table 3.

The dust analysis results in table 2 show that a good repeatability with slight standard variation is achievable by optimised decomposition and determination methods. The element concentration levels (table 3) added to the water were completely re-detected even by using other methods. A quick and low-expenditure analysis of waste waters is possible by using the ICP/AES method.

Analytical chemistry can make its contribution towards re-utilising the major part of dusty waste materials obtained at the facilities of Schott Glaswerke. Thus, these materials, considered lost only 10 years ago, no longer contaminate the environment. Today's recycling rate is of the order of 1 600 kg/d, so this amount no longer presents a danger to the environment. Moreover, analytical chemistry applied to the waste water ensures that only unobjectionable waste waters will be piped into the municipal sewerage.

Finally, the composition of sludges needs to be precisely known and forms the basis of decision for controlled disposal. The question of which percentage is to be delivered to a toxic waste disposal dump, of course, is of great economical significance.

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