

Sampling and Analysis of Emissions in the Rubber Industry

U. Giese, German Institute for Rubber Technology

1. Introduction

During the manufacture and storage of rubber products various gases, vapors and aerosols are emitted due to the complex compound compositions and the concurrent vulcanization that occurs at high temperatures. These emissions consist of volatile components of original compound ingredients such as plasticizers, antioxidants and residual monomers or polymer oligomers as well as primary and secondary reaction products from the crosslinking systems. The formulae and vulcanization conditions of individual substances as well as their origin have been identified in numerous examinations [1-8]. Using these results as a basis, well over a hundred substances are to be expected in the air at the workplace in the rubber industry. These substances are amines, amides, aliphatic/aromatic hydrocarbons, highly volatile sulfur compounds, aldehydes and ketones, phenols and esters. Solvents may also be present depending upon the manufacturing process as these are used for assembly and cleaning. Furthermore, water may be expected in addition to aerosols dependant upon the weather conditions and manufacturing processes. Measurement monitoring of the air at the workplace requires implementation of a measurement method that is able to cope with the extremely complex situation in the rubber industry and can also satisfy the following requirements [9]:

- Sampling period must represent a shift mean value.
- Selectivity for individual dangerous substances.
- Measurement range 1/10 up to 3x limit.
- High precision.

The sampling and analysis procedure is developed from a base of approximately 50 relevant substances that can be expected as emissions and which also have limit values or toxicological ratings [10].

2. Development of a Measurement Method

2.1 Sampling Selectivity

The development and application of a measurement method has the goal of reliably measuring dangerous substances in the air at the workplace in the rubber industry. This requires selective sampling structured on the families to be found by using solid-phase enrichment (adsorbents) as well as considering and possibly necessarily excluding potential negative effects of aerosols, oil gases, cross-sensitivities arising from the complexity of the compounds and humidity by using suitable filters and separator systems [11-14].

Due to the diversity and insensitivity to disturbance effects the principle of active sampling [14] is applied to enriching gas, aerosol and vapor substances on adsorbents.

Various adsorbents [15,16] (polymers, inorganic materials) are examined with regard to their adsorption properties and selectivity for selected substances for the purpose of sampling individual relevant single substances or substance groups.

For selected model substances, inverse gas chromatography was employed to determine adsorption enthalpies and breakdown volumes [13,17] that were used to preselect the combination of substance and adsorption material.

The amount of adsorption enthalpy is dependant upon the interaction between adsorbents and adsorbed substance, whereby the primary influencing factors are polarity and distillation characteristics. Thus, for instance, silica-gel and modified silica-gel in addition to activated carbon are particularly suited as an enrichment material for morpholine. Toluene, on the other hand, is adsorbed excellently on activated carbon.

2.2 Measurement Method Validation

2.2.1 Effectiveness of the Sampling and Analysis Methods

These results were used to examine the suitability of adsorbents by simulating sampling for approx. 50 potentially expected substances, whereby not only enrichment but also the recovery of adsorbed substances using solvent desorption followed by GC or HPLC analysis was uppermost as a simple and universal method.

Simulation of sampling was achieved by using test gases and test gas compounds which were produced by the dynamic vapor pressure saturation process [18]. During these simulation experiments adsorption capacities and breakdown volumes were ascertained in addition to retrieval rates (W) which are calculated in percent from the quotients of the analytically determined concentration and the concentration to be expected theoretically. The retrieval rates show the effectiveness of the enrichment and ensuing desorption.

Table 1 shows a simplified form of an outline of substance groups and the sampling and analysis method which is optimized under the aspect of effectiveness.

Table 1: Determination method chart

Substance/substance group	Collection phase	Recovery (desorption)	Analysis method	W in %
Highly volatile aliphatic and aromatic compounds [20-22]	Activated carbon	Benzyl alcohol	GC-FID (MSD)	90.2 - 100
Amines and amides [23]	Silica-gel ADS	2% KOH in methanol	GC-NPD	86.3 - 100
Highly volatile chlorinated compounds [24]	Activated carbon	Benzyl alcohol	GC-ECD	83.0 - 100
Carbon disulphide, highly volatile ← sulfur compounds [25]	Sampling bag	Acetone	GC-FPD	80.0 - 97.5
Aldehydes (and ketones) [26]	Silica-gel DNPH	Acetonitrile	HPLC-UV	87.2 - 97.5
Low volatility compounds [27]	XAD-2	Acetone	GC-MSD (FID)	94.0 - 98.0
Aerosols [27]	Glass-fiber filter	1,1,2-trichloro-trifluoroethane	FT-IR	94.0 - 98.9

Abbreviations used in Table 1:

DNPH	Dinitrophenylhydrazine	GC	Gas chromatograph
FID	Flame ionization detector	W	Recovery rate
NPD	Nitrogen phosphor detector	UV	Ultraviolet spectrometer
FPD	Flame photometric detector		
HPLC	High-pressure liquid chromatography		
MSD	Mass-selective detector (mass spectrometer)		
FT-IR	Fourier transform infrared spectroscopy		

2.3 Examinations of the Effect of Cross-sensitivities

Cross-sensitivities were examined when sampling selected model substances by using multi-component test gases such as cyclohexane, cyclohexamine, toluene, dimethylformamide, n-octanol and tertiary butylamine [11,12]. The criterion applied when selecting substances was one of representativeness, i.e. the frequency of the emissions to be expected and chemical-physical properties.

Essentially no mutual displacement of substances in the groups in Table 1 occurred on the surface of the selected adsorbents. Merely the simultaneous occurrence of high concentrations of primary aldehydes with amines can result in low values as these substances can react to Schiff's base in the gas phase.

2.4 Effect of Humidity

High humidity sometimes has a negative impact on the effectiveness and absorption capacity of adsorbents on substances to be determined in the air because of the displacement effect of water, which is shown in a low retrieval rate [22-30]. From the physical-chemical aspects an effect is principally to be expected when polar adsorbents are used as water occupies a part of the adsorption centers and blocks them for the analytes. But other effects, such as analytes dissolving in water on the surface of adsorbents, can also have a negative effect upon measurement results.

No negative effect is to be observed for nonpolar substances, such as toluene. The retrieval decreases for polar compounds such as ketones, aldehydes and also for numerous amines.

Apart from a few exceptions humidity can be expected to have a negative effect from approx. 50% and higher relative humidity. In numerous examinations the retrieval rate as a function of humidity was measured for many substances (e.g. acetaldehyde, 2-butanone, cyclohexanone and acetone) and must be taken into account for the analysis result.

2.5 Effect of Plasticizer Vapors and Aerosols

The effect of plasticizer vapors and aerosols upon the determination of gaseous substances was examined using examples of a typical mineral oil plasticizer and a synthetic plasticizer (Di-(2-ethylhexyl)-phthalate) with the aid of simulation tests (test gas compounds) [11,31].

A negative effect upon the accuracy of measurement results only occurred at high aerosol concentrations (approx. 60 mg/m^3) by far exceeding those likely to be encountered in practice. This effect could be rectified by using an additional filter to protect the adsorption tubes from the aerosol.

Overall, the negative effect of aerosols upon the results measured at the workplace is to be neglected in relevant concentration ranges.

3. Sampling Equipment

The interrelationships and extensive surveys upon the selectivity and effectiveness of enrichment materials mentioned above were used as the basis to construct the sampling equipment. This equipment consists essentially of a central pump unit that has a total of six individually controlled intake ducts (defined volume flows) which contain adsorption tubes appropriate to the substances/substance groups to be collected.

Thermal mass flow regulators were used to set and control individual sampling flows. The equipment is only suitable for stationary sampling. The facility to place different adsorption materials in the intake ducts and to adjust the volume flows to be controlled (sampling volumes) individually means that the equipment is extremely adaptable and can be adjusted to match the appropriate relevant conditions.

4. Test Measurements in Simulation Tests and „On Site“

The check on the operation of the developed sampling equipment and the whole procedure was carried out in three stages:

1. Measurements in closed systems
2. Measurements under practice-oriented conditions in the pilot plant
3. Measurements „on site“

Stages 1 and 2 were carried out with known rubber compounds under controlled conditions. A representative example is the vulcanization of a simple tire tread compound using the formulation shown in Table 2.

Table 2: Formulation for a tire tread compound

Component	Amount in phr
Styrene-butadiene rubber	80
Butadiene rubber	20
Carbon black, N 339	80
Aromatic plasticizer	25
Iso-propyl-p-phenyldiamine (IPPD)	1.0
Trimethylquinoline-polymer (TMQ)	1.0
Cyclohexylbenzthiazolsulfenamide (CBS) ¹⁾	1.5
Diphenylguanidine (DPG)	0.5
Sulfur	2

¹⁾ alternatively tertiary butylbenzthiazolsulfenamide (TBBS)

The vulcanization time (t_{90}) is 6.5 minutes at a temperature of 170°C.

Measurements in the closed system:

The examination of vulcanization fumes using the „Dynamic Headspace Method“ [3,32] resulted in the chromatogram in Fig. 1 [3,32]. In the „Dynamic Headspace Method“ vulcanization is carried out in a closed system and all of the released substances are passed into the analysis system loss-free. The analysis system is one linking gas chromatography with mass spectroscopy (GC-MS). The chromatogram shows the maximum expected emissions when vulcanizing the tire tread compound shown above.

The front part of the chromatogram (lower retention times) is characterized by the mostly very volatile primary and secondary reaction products produced in the crosslinking system. Low volatility components such as antidegradants and high carbohydrates occur in the rear portion of the chromatogram. Quantitative analysis of individual components is not possible or full of errors due to the sometimes insufficient fractionation.

Measurements under practice-oriented conditions in the pilot plant:

Sampling and analysis of vulcanization fumes in accordance with the concept of the compound shown above presented in section 2 under pilot plant conditions results in well disintegrated chromatograms of components of individual families which permits precise quantification of relevant single substances.

The main components cyclohexamine and aniline as typical primary CBS or primarily DPG reaction products are to be assigned to the acceleration system.

The extremely selective and sensitive sampling of ketones and aldehydes using chemisorption and derivatization to the corresponding hydrazones [25] followed by HPLC analysis produces three identified and quantified compounds. These are acetaldehyde, acetone and cyclohexanone. Acetaldehyde occurs in only minor concentrations compared to the other two compounds. Its origin has not been clarified. Acetone is produced by isopropylamine oxidation which is an IPPD dissociation product. Since isopropylamine was not detected during analysis of the amines of the silica-gel ADS, transformation must be complete. Cyclohexanone forms as a secondary reaction product from the action of oxygen on cyclohexamine which, as stated above, is to be assigned to the CBS.

Low volatility components (aerosols, vapors) are collected by the combination of glass-fiber filter/XAD-2 tubes.

Gas chromatographic analysis of the filter eluate produces exclusively a mixture of high-boiling components from the crosslinking system such as IPPD or methylthiobenzthiazole. Quantitative analysis takes place as stated above as a summation using an FT-IR spectroscopic method [26]. Substances that pass through the filter are adsorbed unselectively by XAD-2. XAD-2 is a polymer based upon polystyrene divinylbenzene and is characterized by an advantageous low specific surface for the unselective adsorption of high-boiling components [33]. GC-MS analysis of the acetone eluate is used to identify numerous saturated and unsaturated hydrocarbons with a polymer and plasticizer origin in addition to high-boiling reaction products of the crosslinking system such as benzthiazole or N-benzylcyclohexylamine.

Overall one can say that comparison of the results of laboratory experiments (Dynamic Headspace Method) and of the pilot plant tests show very good correlation and the developed selective sampling procedure showed itself to be very suitable.

Measurements „on site“:

The third step of the testing phase, „on site“ measurements, was carried out at locations in the tire industry and at manufacturers of technical rubber goods. The areas of extrusion, vulcanization, cool-down and storage of car tire production were selected at a total of five tire manufacturers. The recipes and manufacturing processes are very similar to one another due to similar product requirements in this branch of industry, so that a similar spectrum of emitted components is to be expected.

Tertiary butylamine and aniline were typically found at nearly all tire manufacturers. Both components are reaction products of accelerators that are typical in the tire industry. Tertiary butylamine is formed from tertiary butylamin-benzthiazolsulfenamide (TBBS), a „nitrosamine-free“ accelerator. Aniline is released in traces of benzthiazolsulfenamides, but mainly from diphenylguanidine (DPG), a synergistically acting and also „nitrosamine-free“ accelerator.

In all cases concentrations of these substances were below the limit of determination, i.e. for tertiary butylamine under 0.05 mg/m^3 and for aniline under 0.03 mg/m^3 and therefore far under the applicable limit values. Evaluations for highly-volatile compounds at some locations show a wide range of aliphatic, cyclic and aromatic hydrocarbons with carbon numbers of principally C_5 to C_{10} . The spectrum of these compounds is partly typical for benzenes. Concentrations of these components which are counted as being solvents are very different depending upon individual company processes. Concentrations of 1.1 mg/m^3 were measured for hexane, whereas the values for heptane were between 6.1 to 114 mg/m^3 and those for octane between approx. 0.1 and 125 mg/m^3 . Concentrations of aromatic solvents, such as xylene or ethylbenzene are far lower than those of aliphatic components and lay in the range of 3 mg/m^3 and significantly below. It is notable that the highest concentrations of solvents tend to occur in the area of tread extrusion. The substance styrene, which can also potentially stem from solvent compounds but is also prevalent as a residual monomer in the SBR, was only ascertained in two companies with concentration levels of below 0.29 mg/m^3 . A comparison of concentrations that were measured of single highly-volatile hydrocarbons with, for instance, the limit values that apply in Germany [10], show that all lay far under the limit values.

It is also of interest in the results that components from the group of chlorinated highly-volatile solvents, such as methylene chloride or tetrachloroethylene, were found. However, apart from a few exceptions, the concentrations are to be placed in the area of ubiquitous loading. Individual higher values can mostly be assigned to exceptional instances.

Oxygenated compounds from the group of aldehydes and ketones as well as highly-volatile sulfur compounds are insignificant in the environmental air at tire manufacturing according to the measured results. In individual cases low concentrations of pentanone and 2-butanone were detected in the tread extrusion area.

An analysis of measured concentrations of higher-boiling components (aerosols and vapors) show concentrations below 0.4 mg/m^3 over all the measurement sites.

Measurements at manufacturers of technical rubber goods are more interesting due to the diversity of formulations used and the resulting wide range of vapor and gaseous emissions. The work areas in compound manufacturing, vulcanization processes (autoclave, press, UHF) were considered here.

Essentially a wide diversity of typical single components from the following substance groups were found in field tests:

- Highly-volatile hydrocarbons (solvents),
- Amines (accelerator reaction products),
- Aldehydes/ketones (reaction products of peroxidic crosslinking systems and formaldehyde from bonding systems),
- Chlorinated hydrocarbons (solvents, cleaning agents),
- Aerosols, low volatility vapors.

With regard to highly-volatile accelerator reaction products from the group of nitrogenous and sulfurous compounds, merely morpholine from the accelerator oxydimethylenebenzthiazolsulfenamide (MBS) or from the sulfur donors oxydiethylenedi(thiocarbamyl-N'-oxydiethylenesulfenamide (OTOS), cyclohexamine from CBS and diethylamine and dibutylamine from the correspondingly substituted thiurams and dithiocarbamates with concentrations of under 0.2 mg/m^3 were detected, i.e. way below the existing limit values. With regard to highly-volatile hydrocarbons, mainly toluene with low values under 35 mg/m^3 and traces of aliphatic hydrocarbons were identified.

Similar to measurements taken at tire manufacturers, chlorinated solvents were also found at technical rubber goods production sites. These also lay in the range of ubiquitous concentration and in single cases could be traced back to a special procedure. This makes the measured values plausible, even if this type of solvent is not used for the actual production of rubber.

Aldehydes and ketones, such as butanone, were detected as a result of peroxidic crosslinking which is sometimes normal in the field of technical rubber goods. However, the concentrations are extraordinarily low, as is also the case with crosslinking reaction products of the measurements stated above, and were under 0.02 mg/m^3 . Vapor-forming low volatility substances and aerosols have concentrations far below a total of 1 mg/m^3 at the analyzed measurement sites.

In total, the result of the field tests is that depending upon local conditions, recipes and manufacturing processes, substances of the groups stated above occur in different, often very small concentrations far under applicable limit values. Higher concentrations of solvents were registered only in individual cases.

The main reason for the low values is that in all measurement ranges that were considered in both the tire industry as well as at manufacturers of technical rubber goods, effective suction systems are installed so that workplace exposure is normally to be classified as being low. This result is in line with the trend shown in a Swedish study [34].

The substances identified for all measurements performed can be plausibly traced back to the formulations and processes, as far as is known. Plausibility measurements in the form of summations of all emitted substances can be interpreted as being in line with individual determinations of substances. The function of the overall procedure and the sampling equipment was thereby successfully demonstrated in field tests.

5. Summary

An efficient sampling and analysis method for monitoring air at the workplace in the rubber industry has been developed based upon the currently applicable regulations such as the hazardous substances ordinance in Germany as well as technical regulations. The procedure, consisting of stationary sampling and central analysis, is validated for a total of approx. 50 single substances and its suitability has been checked in extensive laboratory experiments and practical tests.

In the final development phase, field tests in the tire industry and at manufacturers of technical rubber goods, with due consideration of diverse recipes and manufacturing processes in particular, have demonstrated the reliable function of the procedure and the accuracy of the results.

With regard to workplace exposure, it was determined for both the analyzed measurement sites as well as the manufacture of technical rubber goods that concentrations of single components from substance groups of highly-volatile and chlorinated hydrocarbons, of aldehydes and ketones, of amines and amides, of sulfurous highly-volatile substances and vapors and aerosols were far below applicable limit values due to the recipe structure and effective ventilation systems.

Note of Thanks:

We would like to express our gratitude to the Professional Association of the Chemical Industry, Heidelberg, for its generous financial support.

6. References:

- [1] R. H. Schuster, H. Linde and G. Wünsch, *Kautsch. Gummi Kunstst.* **44** (1991) 222
- [2] R. H. Schuster, „Messung und Interpretation von Vulkanisationsdämpfen“, presentation at the VDI Convention, Brunswick (1992)
- [3] J. Zietlow, R. H. Schuster, R. Badura and G. Wünsch, *Gummi Fasern Kunstst. (GAK)* **44** (1991) 318
- [4] B. G. Willoughby and G. Lawson, *Environ-Health Persp.* **17** (1976) 45
- [5] R. Liekefeld, R. H. Schuster and G. Wünsch, *Kautsch. Gummi Kunstst.* **44** (1991) 514
- [6] V. Cocheo, M. L. Bellomo and G. G. Bombi, *Am. Ind. Hyg. Ass. J.* **44** (1983) 521
- [7] B. G. Willoughby, *Rub. Chem. Technol.* **54** (1981) 311
- [8] B. G. Willoughby, *Europ. Rubber J.* **166** (3) (1984) 49
- [9] Technische Regel für Gefahrstoffe (TRGS) 402, (Sept. 1993 edition), *Bundesarbeitsblatt* (1986)
- [10] Technische Regel für Gefahrstoffe (TRGS) 900, *Bundesarbeitsblatt*, April (1995)
- [11] I. Kollat, thesis, University of Hanover (1992)
- [12] T. Will, thesis, University of Hanover (1994)

- [13] U. Giese, „Probenahme und Analytik von Vulkanisationsdämpfen in der Gummiindustrie“, presentation at the DIK Workshop, May (1996)
- [14] H. Siekmann and H. Blome, Staub Reinhaltung der Luft **48** (1988) 89
- [15] U. Giese, in: DFG, Luftanalysen, Vol. 1, Chap. 8, 9. Versin (1994) 87
- [16] K. Figge, N. Rabel and A. Wieck, Fresenius Z. Anal. Chemie **327** (1987) 261
- [17] I. Stanetzek, U. Giese, R. H. Schuster and G. Wünsch, Am. Indust. Hygiene Ass. J. **57** (1996) 128
- [18] H. Weber and H. Stenner, A. Kettrup, Fresenius Z. Anal. Chemie **325** (1986) 64
- [19] NIOSH: Manual of analytical methods, from Gov. Rep. Announce, Index U.S. (1990)
- [20] A. Schütz and W. Coenen: Messungen von Gefahrstoffen, Expositionsermittlung bei chemischen und biologischen Einwirkungen, publisher BIA: Erich Schmidt Verlag, Bielefeld (1990)
- [21] J. Rudling, J. of Chromatography **503** (1990) 33
- [22] K. H. Pannwitz, Bestimmung der Amine am Arbeitsplatz, Drägerheft **11/12** (1988) 342
- [23] A. Essing and F. Umland, Fresenius Z. Anal. Chemie **321** (1985) 544
- [24] Y. K. Lau, Environmental Monitoring and Assessment **13** (1989) 69
- [25] R. R. Arnts and S. B. Tejada, Environ. Sci. Technol. **23** (1989) 1428
- [26] D. Breuer and W. Pfeifer, Staub Reinhaltung der Luft **49** (1989) 353
- [27] D. M. Werner, Am. Indust. Hygiene Ass. J. **46** (10) (1985) 585
- [28] K. Andersson et. al., Chemosphere **13** (3) (1984) 437
- [29] G. O. Wood, Am. Indust. Hygiene Ass. J. **48** (12) (1987) 622
- [30] Y. H. Yonn and J. A. Nelson, Am. Indust. Hygiene Ass. J. **49** (7) (1988) 325
- [31] T. Will and U. Giese, Kautsch. Gummi Kunstst. **49** (1996) 200
- [32] J. Zietlow, R. H. Schuster, R. Badura and G. Wünsch, Gummi Asbest Kunstst. (GAK) **44** (1991) 318
- [33] J. S. Fritz and R. C. Chang, Analytical Chemistry **46** (1974) 938
- [34] J. Asplund, Curing Fumes - A Large-Scale Study, Kautsch. Gummi Kunstst. **48** (1995) 276