

**DETERMINATION OF AKD SIZING AGENTS IN PAPERMAKING SYSTEMS
BY GAS CHROMATOGRAPHY****Janja Zule, Jožica Dolenc***Pulp and Paper Institute, Bogišičeva 8, 1000 Ljubljana, Slovenia**Received 12-11-2002***Abstract**

Analytical procedure for determination of bound and unbound forms of alkylketene dimer (AKD) sizing agent in paper is presented. The overall sizing efficiency depends on their distribution in paper structure. Individual AKD portions were separated from each other, hydrolysed to the corresponding ketones and evaluated by GC. The method was developed on well defined reference paper samples. Some papermaking process waters were also evaluated for AKD content after extraction of hydrolysed solid residue.

Introduction

Sizing is a process to produce paper of more hydrophobic character, which becomes, due to its enhanced liquid penetration resistance, suitable for printing purposes. Different chemicals may be used as sizing agents. Widely applied are rosin sizes, where the active component is aluminium resinate and the sizing effect is achieved by electrostatic interactions between cellulosic surface and highly hydrophobic agent. They function only in acidic papermaking conditions, unless aluminium sulphate is replaced by polyaluminium chloride. Due to the availability of inexpensive calcium carbonate to be used as a filler and consecutive higher chemical stability of neutral papers, many papermills have changed from acidic to neutral or slightly alkaline pH of the system. As a consequence, different type of sizing agents had to be introduced, which would meet new requirements. Most suitable proved to be alkylketene dimers (AKD), alkenyl succinic anhydride (ASA), carbamoyl chloride and stearic acid anhydride. All of them belong to the class of reactive sizes, as they chemically react with cellulosic fibers to render their surface more water repellent.^{1,2}

For the last few years AKD has been most widely used reactive sizing agent in the production of high quality printing papers. It is manufactured from a mixture of higher fatty acid chlorides, mainly palmitic and stearic. The corresponding alkylketene dimers have lactone rings which can easily undergo chemical reactions. Their chemical structure is presented in Figure 1.

In papermills AKD is used in the form of aqueous dispersion with particle sizes between 0.2 and 2 μm in diameter.¹ Such dispersions are usually stabilized by addition of cationic starch.

The sizing process takes place during drying of paper sheets and is strongly dependent on different technological parameters like applied raw materials, pH value of fiber suspension, time, temperature and method of drying.

The proposed mechanism of AKD sizing is the formation of β -keto esters between AKD and free OH groups on cellulosic fibers. Ring opening always occurs at the acyl-oxygen bond. (Figure 1).^{3,4}

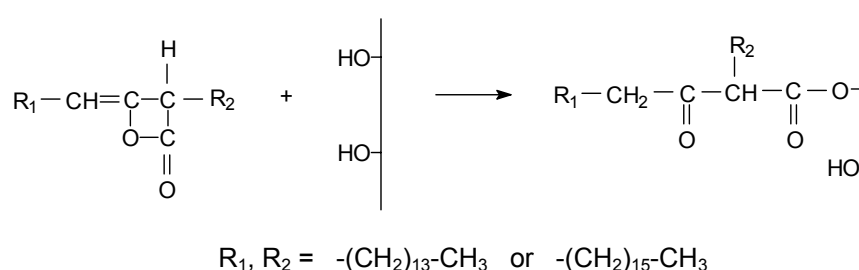


Figure 1: Reaction of alkylketene dimers with OH groups on cellulosic molecule.

However, it has been established that not all of AKD chemically reacts with fibers. Some of it may undergo hydrolysis in water to form unstable β -keto acids, which decarboxylate to the corresponding ketones (Figure 2).^{3,4}

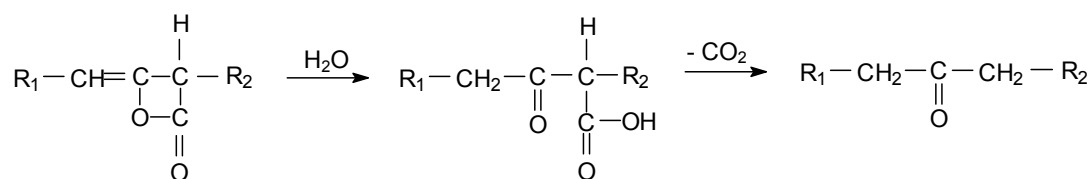


Figure 2: Hydrolysis of alkylketene dimer in water medium.

Still another portion remains unreacted and adsorbs onto fibers in its original form. The sizing effect depends mainly on the quantity of chemically bound AKD in paper, while the role of unbound forms, that is ketones and dimers, is still not clear, though it is generally considered that they represent the loss of sizing efficiency.^{5,6}

Ideally, all AKD should be retained in paper structure, but that is usually not the case, as some may be also found in process waters and in the form of sticky deposits on machine equipment and as such represents an important source of papermaking systems contamination.⁷

Determination of various forms of AKD in paper can not be performed straightforwardly by simple laboratory methods, however there have been some reports of detailed chemical analyses by GC, GC-MS, HPLC, UV/VIS spectrophotometry, NMR and FTIR spectrometry and pyrolysis GC.^{8, 9, 10, 11, 12, 13}

The aim of our investigation was to introduce appropriate analytical procedure for quantitative evaluation of bound and unbound portion of AKD in paper samples and total AKD in process waters. Different forms were first separated and removed from paper, then they were hydrolyzed to the corresponding ketones, if necessary and finally evaluated by GC. The analytical method was developed on well defined reference paper. Typical process water samples were also analyzed for AKD content.

Experimental

Reference AKD sized paper was manufactured on a lab sheet former according to the standard procedure ISO 5269-1. The sizing agent used was a commercial AKD dispersion produced by Melamin. All solvents and chemicals used in analytical experiments were of reagent grade.

Preparation of chromatographic standards

Solid AKD, provided by the same producer as dispersion, was used for the preparation of ketone mixture that served as chromatographic standard. About 5 g of AKD wax was refluxed with 6M HCl for 2 h. Water was removed by filtration immediately after cooling of the mixture to room temperature. The solid product (impure ketones) was dissolved in hot methylene chloride, quickly filtered and finally cooled to precipitate the ketones. The recrystallization was repeated several times. The purity of the product was verified by IR spectroscopy (1705 and 1460 cm^{-1}) and GC (purity of ketone standard was 98%). The standard is applicable for the analysis of any AKD sized paper if the sum of all three ketone peaks is used for the calculation of AKD concentration.⁹

Paper analysis

Analytical procedure for the determination of bound and unbound AKD in paper samples and total AKD in process water samples is presented in Figure 3.

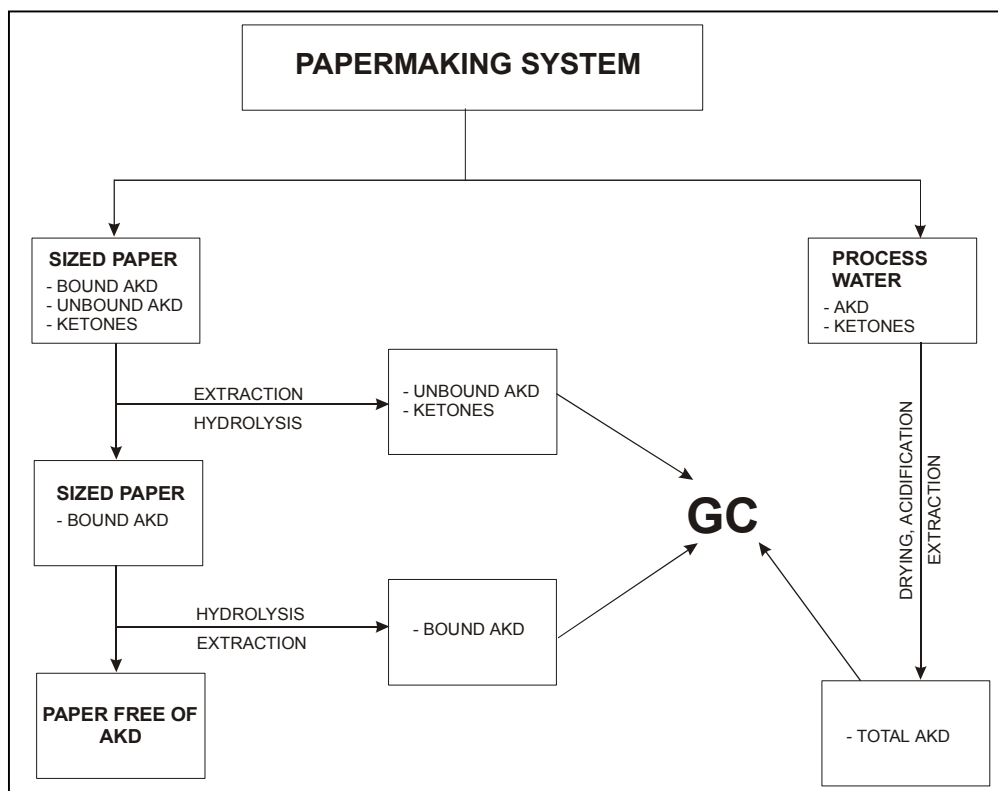


Figure 3: Analytical scheme for AKD determination in papermaking systems.

It is essential that all AKD is converted to the corresponding ketone form by hydrolysis, prior to GC analysis. Several hydrolyzing agents (HCl, NaOH, 0.5 M KOH in ethanol, Na₂CO₃) were tested during the preliminary experiments, however 6 M HCl with addition of iso-octane (3 : 1, v/v) proved to be the most efficient. The special feature of the procedure is the combination of hydrolysis and extraction steps. As they are performed simultaneously, the efficiency of the method is greatly increased.

1. Determination of unbound AKD

About 10 g of paper was cut into small pieces and weighed. It was Soxhlet extracted with 150 mL of hexane for 8 h. The obtained extract was evaporated to dryness. The residue was refluxed with 10 mL of 6 M HCl for 1 h. The hydrolysate was

extracted in testing tubes with 3 x 4 mL of warm hexane (approximately 40 °C). The extracts were collected and concentrated to the final volume of 1 mL. The content of ketones was evaluated by GC.

2. Determination of bound AKD

The remaining hexane extracted paper was dried up, after which 150 mL of 6 M HCl and 50 mL of iso-octane were added. The mixture was refluxed 2 h, filtered through glass filter and the remaining fibers were washed with 3 x 25 mL of warm hexane (approximately 40 °C). Organic and water phases of filtrate were separated in a separating funnel. Organic phase was concentrated to the final volume of 1 mL. The content of ketones was evaluated by GC.

Water analysis

40 mL of process water was acidified with a drop of conc. H₂SO₄, evaporated to dryness at 25 °C in vacuum desiccator. The residue was extracted with 3 x 5 mL of warm hexane. The collected extracts were concentrated to the final volume of 200 µL and analysed by GC.

Gas chromatography

GC analyses were performed on HP 5890 at the following experimental conditions: capillary column SPB-1 (15 m) from Supelco, injector temp. 350 °C, split ratio 1:15, init. oven temp. 230 °C (0 min), heating rate 5 °C/min, final oven temp. 300 °C (10 min), det. FID temp. 350 °C, N₂ flow 1.5 mL/min. Major ketone peaks were integrated and their concentrations calculated from the calibration curve of the corresponding standard ketone mixture. Calibration was made by using the following concentrations of standard ketone mixture in hexane: 0.1; 0.5; 1; 2.5; 5; 7.5 and 10 mg/mL.

The overall analytical procedure for the determination of bound and unbound AKD in reference paper sample was repeated 3 times. All GC measurements were performed in 6 parallels.

Results and discussion

All the chromatograms obtained showed essentially the same picture, that is three prominent peaks of the following ketones: $C_{16}COC_{16}$, $C_{16}COC_{18}$ and $C_{18}COC_{18}$, which was somehow expected as AKD had been synthesized from palmitic and stearic acid chlorides.

Original form of alkylketene dimers can not be detected by GC due to its low volatility, so the product has to be first hydrolysed to ketone form, which is more suitable for quantification. Calibration graph was prepared by plotting the sum of three ketone peak areas against AKD concentration and is presented by the equation and correlation coefficient ($y = 7E+06x - 408600$; $R^2 = 0.9997$).

A typical chromatogram of bound portion of AKD, obtained after acid hydrolysis of preextracted reference paper sample is shown in Figure 4.

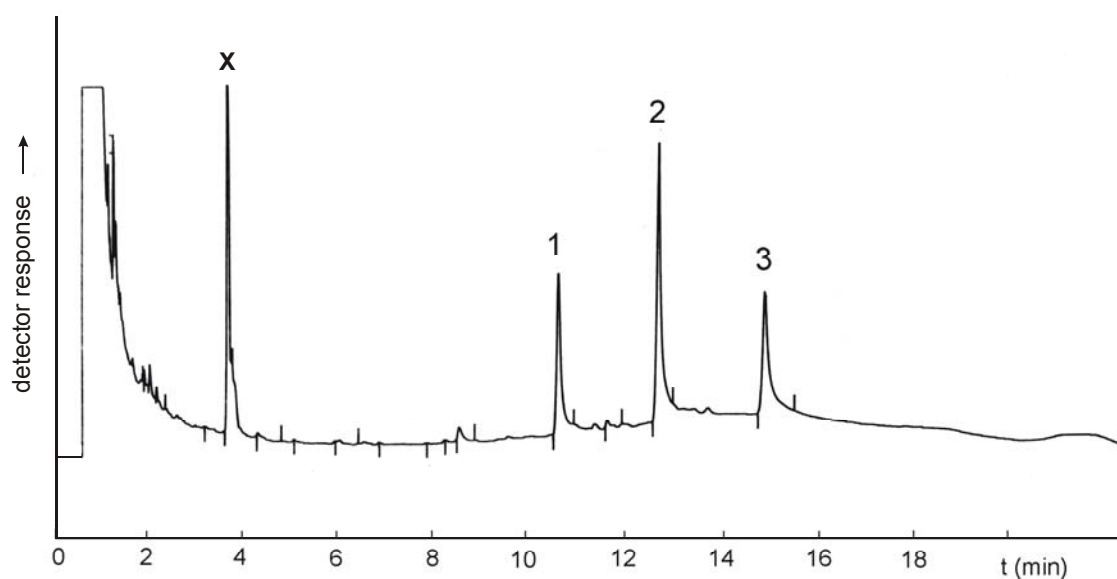


Figure 4: Gas chromatogram of bound AKD in paper sample
(1 - $C_{16}COC_{16}$, 2 - $C_{16}COC_{18}$, 3 - $C_{18}COC_{18}$).

X is unidentified component, extracted from the paper sample and as such it is not present in chromatograms of the standard. The method proved to be very selective, as there were no interfering peaks in any of the chromatograms. The average values of individual determinations with standard deviations ($n = 6$) are collected in Table 1.

Table 1: AKD determination in reference paper sample.

Determination	Bound AKD mg/g	Unbound AKD mg/g	AKD* mg/g
1	0.107 ± 0.005	0.880 ± 0.020	0.987 ± 0.021
2	0.096 ± 0.005	0.757 ± 0.034	0.853 ± 0.034
3	0.103 ± 0.004	0.817 ± 0.020	0.920 ± 0.020

* the values are the sum of bound and unbound portions of AKD

The obtained values demonstrated very good repeatability for bound AKD, while there were slightly greater deviations from the average in case of unbound sizing agent determinations. The differences in the measured quantities of unbound AKD could be partly ascribed to the inhomogenities in the paper structure. The detection limit was under specified chromatographic conditions 0.02 mg/mL (experimentally estimated by appropriate standard solution), which in other terms represents 2 µg AKD per g of oven dry paper.

Average total AKD (*Table 1) recovery was 92%, calculated from the known addition of active agent, which was 1 mg/g of paper.

The most striking fact was that bound portion of AKD represented only about 11% of the total AKD recovered, and the reason for such distribution could be very low AKD addition. However, according to the literature, the quantity of bound portion rarely exceeds 50%, even in optimal technological conditions.¹⁴

The analyses of industrial process waters showed that the extraction of ketones (all AKD in process waters is in hydrolysed form) could not be performed directly, because of strong interaction from numerous papermaking chemicals. The same water sample was analysed using liquid liquid (direct) and solid liquid extraction. The obtained value was several times lower in the first case. The extraction and analysis of dried samples gave on the other hand repeatable and higher values. The concentration range of AKD was between 0.01 and 0.04 mg/L.

Conclusions

The newly developed method for determination of bound and unbound forms of AKD sizing agent in paper enables better understanding of sizing mechanisms in

different technological environments. The obtained results exhibit fairly good reproducibility and reliability and match well with simple laboratory tests of sizing efficiency. The method is suitable for performing routine determinations of AKD distribution in industrial paper samples. Systematic analyses have also confirmed previous assumptions that the most important portion of sizing agent is the one that is chemically bound to cellulosic fibres, though it is not necessarily predominant.

Acknowledgements

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Povzetek

Predstavljen je analitski postopek za določitev kemijsko vezane in nevezane oblike alkil ketenskih dimer oz. AKD klejiva v papirju. Temelji na izolaciji in karakterizaciji estersko vezanega dela ter adsorbiranih dimerov in njihovih hidroliznih produktov ketonov. Od njihovega medsebojnega razmerja oz. porazdelitve v papirju je odvisen učinek klejenja. Postopek predvideva pretvorbo vseh oblik klejiva v ketone, ki se jih kvantitativno ovrednoti s pomočjo plinske kromatografije. Metoda je bila vpeljana na osnovi analiz referenčnega papirnega vzorca.

V članku je predstavljen tudi postopek določitve ostankov klejiva z ekstrakcijo hidroliziranega suhega ostanka papirniških procesnih vod.