Short thesis for the degree of doctor of philosophy (PhD)

Investigation of the formation of polyurethanes and their products by mass spectrometric methods

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I Introduction and goals

Mass spectrometry (MS) can be used to determine the quality and quantity of organic and inorganic compounds. Due to its unique sensitivity, limit of detection, small sample size, speed, and diverse application, it plays an important role in kinetic analysis. Using soft ionization techniques high molecular weight compounds can be studied, so molecular weight of polymers and proteins can be determined quickly and easily. In tandem mass spectrometry (MS/MS) the precursor ion is selected and activated. Fragmentation of the precursor ion and its fragmentation pathway provides structural information.

Polyurethanes (PUs) are one of the most widely used polymers. The nucleophilic addition of an isocyanate and an alcohol is the most important reaction of polyurethanes manufacturing. We studied the kinetics of the reaction of diisocyanates and monofunctional alcohol, with two or three functional groups (OH) by the means of mass spectrometric methods. 4,4‘-diphenylmethane diisocyanate (MDI) and 2,4-toluene diisocyanate (2,4-TDI) were reacted with different alcohols (butan-1-ol, butan-2-ol, diethylene glycol monomethyl ether - DEGME), so the kinetic description of reactions corresponds to the pseudo first order model. Thus, we could compare the reactivity of the two diisocyanate compounds towards alcohols. For our study we used ESI-MS any HPLC-UV methods. Furthermore, the MDI was reacted with polymer-diols, including polypropylene glycol (PPG), polytetrahydrofuran (PTHF), polycaprolactone diol (PCLD) and a triol polypropylene glycol glycerol triether (PPG_GL). The reactions of MDI with different polyols was also studied by MALDI-TOF mass spectrometry, to determine the reactivity of hydroxyl groups of polymers. The reactions of 4,4'-MDI with alcohols (ROH) (a) and the structure of products after the components reacted with methanol (b) are shown in **Figure 1**. where *A* is the reactant compound, *B* is the single reacted diisocyanate, and *C* is the final product.

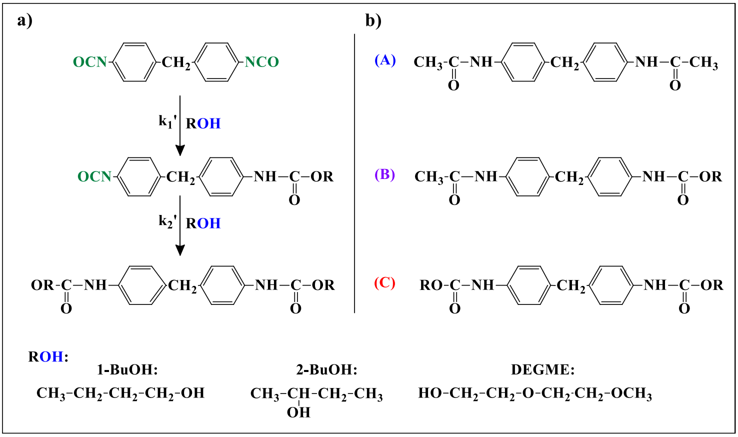

Figure 1. The reactions of 4,4'-MDI with alcohols (ROH) (a) and the products obtained after quenching the reaction mixture with methanol (b)

Furthermore, we also examined polyurethane-based commercially available clothing products that containing elastane using the DART-MS technique. Elastane, is one of the products of the PU industry. Our goals were the quick and non-destructive determination of the residue of chemicals from the surface. Among the identified compounds we can find many substances harmful to health. Textile products can come into direct contact with human skin and are easily released into the environment with domestic wastewater.

II Experimental

1. Chemicals

4,4’-MDI, 2,4-TDI, butan-2-ol, DEGME, PCLD (M_n = 2000 g/mol), PTHF (M_n = 1000 g/mol), THF, acetonitril (HPLC grade) and toluene were received from Sigma Aldrich (Taufkirchen, Germany). PPG (M_n = 2000 g/mol) and PPG-GL (M_n = 1000 g/mol; Rokopol G1000) were obtained from BorsodChem (Kazincbarcika, Hungary) and PCC Rokita SA (Brzeg Dolny, Poland) respectively. Butan-1-ol and methanol were purchased from Merck (Darmstadt, Germany) and VWR International (Leuven, Belgium) respectively. Water was purified by a Direct-Q water system (Millipore, Molsheim, France).

In the study of textile products, we analysed 15 commercially available textile items of different types, materials, colours and countries of origin. Some of these investigated samples contained elastane, which is one of the products of the PU industry. The main characteristics of the samples are summarized in **Table 1**.

Table 1. The main characteristics of the textile samples

No.	Type	Material	Colour
1	Sweater	100 % polyester	Grey
2	Shirt	80 % cotton, 20 % polyester	Black
3	Socks	100 % cotton	Black
4	Jeans	100 % cotton	Blue
5	T-shirt	85 % polyester, 15 % elastane	Blue
6	Shirt	100 % cotton	Brown
7	Skirt	50 % acrylic, 40 % cotton, 10 % elastane	Black
8	Shirt	100 % cotton	Black
9	T-shirt	95 % cotton, 5 % elastane	Purple
10	Cap	100 % acrylic	Grey
11	Socks	44 % polyamide, 39 % polypropylene, 11 % cotton, 4 % polyester, 2 % elastane	Blue
12	Socks	90 % cotton, 5 % polyamide, 5 % elastane	Black
13	Socks	80 % cotton, 17 % polyamide, 3 % elastane	Grey
14	Socks	100 % cotton	Blue
15	Shirt	100 % cotton	Grey

2. Instrumentals

The distribution of the products of the reaction of 4,4'-MDI with alcohols was studied with a WatersAlliance HPLC instrument (Waters 2695 Separation module). For separation an AgilentZorbax SB-C18 type column was used (length: 75 mm, diameter: 4,6 mm and particle size: 3,5 µm). Temperature of column module was kept at 40°C. The analytes were detected at 245 nm. (Waters 2996 PDA detector).

The MS and MS/MS measurements were performed using a MicroTOF-Q type Qq-TOF MS instrument (Bruker Daltonik, Bremen, Germany) equipped with an ESI source. The ions were detected in the positive ion mode. The spray voltage was set to 4 kV. The temperature of the drying gas (N_2) was kept at 180°C.

To monitor the reaction of 4,4'-MDI with polyols MALDI-TOF MS measurements were performed by a Bruker BIFLEX III™ mass spectrometer equipped with a time-of-flight (TOF) mass analyzer. The positive ions were detected in the reflectron mode (20 kV).

The recorded mass spectra were evaluated by means of DataAnalysis 3.4 software from Bruker.

For the investigation of textile items, a DART-SVP ion source was used, which was connected to the previously mentioned Bruker Daltonics MicroTOF-Q type QqTOF-MS. No sample preparation was required.The precursor ions for MS/MS were selected with an isolation width of 4 *m/z* unit. nitrogen gas was used as the collision gas and the collision energies of 6 eV and 35 eV were used. The pressure in the collision cell was determined to be $\sim 1.2 \cdot 10^{-2}$ mbar.

3. Sample preparation

For the reactions of 4,4'-MDI and 2,4-TDI with alcohols into a flask of 10 ml, dry toluene (5 ml) and calculated amount of diisocyanate were introduced under nitrogen atmosphere. The flask was thermostated at a predetermined temperature. After addition of the calculated amount of the alcohol and the reaction mixture was further diluted with dry toluene to obtain a reaction volume of 10 ml. The initial concentrations of the diisocyanates and the alcohols were 0.01 M and 0.65 M, respectively. For liquid chromatographic and mass spectrometric investigation, after predetermined time intervals, samples of 10 μl were taken out from the reaction mixture and added to methanol to quench the unreacted isocyanate groups.

Samples for the HPLC-UV measurement were prepared as follows: 10 μl sample from the solution made by diluting 10 μl reaction mixture with methanol to 1000 μl (HPLC sample) was injected into the chromatograph system. Samples for the ESI-QTOF MS measurement were prepared as follows: to a 5 ml of HPLC sample 10 μl sodium chloride solution (20 mM) was added and the mixture was further diluted with methanol to 1000 µl.

For the reaction of 4,4'-MDI with polyols, into a flask of 5 ml, dry toluene (3 ml) and calculated amount of MDI were introduced under nitrogen atmosphere. The flask was thermostated at 80°C. The reactions were started by addition of the calculated amount of the corresponding polymer polyols dissolved in toluene of 1 ml. The reaction mixture was further diluted with toluene to obtain a reaction volume of 5 ml. The initial concentrations of MDI and the polymer polyols were 0.32 M and 0.01 M, respectively. For the MALDI-TOF MS investigations, after predetermined time intervals, samples of 100 µl were taken out from the reaction mixture and added to a mixture of methanol/tetrahydrofuran (2 : 1 v/v) to quench the unreacted isocyanate groups (analyte). Samples for the MALDI-TOF MS measurement were prepared as follows: 2,5-dihydroxy benzoic acid (DHB) matrix was dissolved in tetrahydrofuran at a concentration of 20 mg/ml. Analyte samples were obtained by mixing 100 µl reaction mixture with methanol (400 µl) and tetrahydrofuran (200 µl) and sodium trifluoroacetate dissolved in tetrahydrofuran at a concentration of 5 mg/ml (used as the ionization agent). The solutions were mixed in a 10 : 2 : 1 (v/v) ratio (matrix/analyte/cationization agent). A volume of 0.5 µl of the solution was deposited onto a metal sample plate and allowed to air-dry. Samples for the ESI-MS and ESI-MS/MS measurements were prepared using 10µl of methanol-quenched reaction mixtures obtained at different reaction times and diluted with methanol to 1000 µl.

The DART ion source allowed us to study individual textile items without sample preparation and sample destruction. The solid samples were manually introduced into the DART gas stream.

III New scientific results

1. Study of the formation of urethane bonds formed during the reaction of diisocyanates and alcohols

1.1. We have demonstrated that using the intensity of adduct ions generated under ESI conditions, we can quickly and efficiently monitor the product distribution of the reactions between diisocyanates and alcohols. The reactivity of MDI and TDI diisocyanates to alcohols was determined and compared. Based on our results, the molar fraction values obtained from the data of HPLC-UV and ESI-MS measurements were practically the same in all sample solutions. **Figure 2** shows the distribution of the molar fraction as a function of time measured for 4,4'-MDI-butan-1-ol for components B (one reacted isocyanate group) and C (after the reaction of both isocyanate groups) using both detection methods. The blue and red symbols show the data of obtained from ESI-MS and HPLC-UV measurements, respectively. A high molar ratio of alcohol was used in the reactions to provide pseudo-first-order kinetics. The solid curves shown in Figure 2 were determined by fitting, where the pseudo first-order reaction rate constants *k* were used as variable parameters.

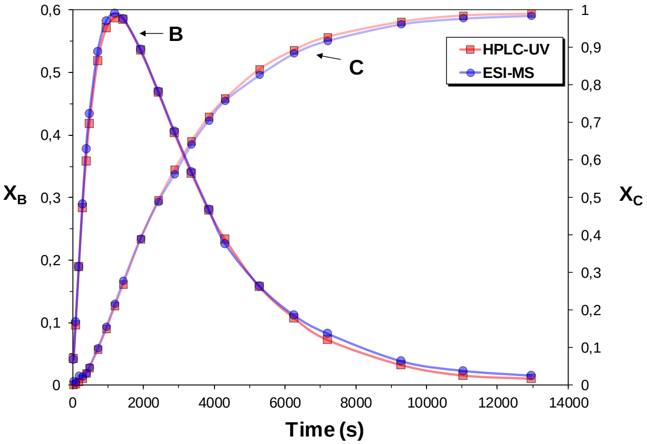

Figure 2 Comparison of the ESI-MS and LC-UV results for the product distributions versus reaction time obtained in the MDI-1-butanol reaction at 45°C. Initial concentrations: $[\mathrm{MDI}]_o$=0.01M and $[\text{butan-1-ol}]_o$=0.65M.

1.2. We proved that the first isocyanate group of 4,4'-MDI reacts with the hydroxyl group of the alcohol approximately 1.5 times faster than the second isocyanate group. It was also shown that no side reactions occurred under our reaction conditions. We examined, how the reactivities of the MDI and TDI isocyanate groups change after addition of alcohol to the first isocyanate group. It was confirmed that the reactivity of both isocyanate group decreases after the carbamate formation. The apparent activation energy of the reaction of MDI and TDI diisocyanates with alcohols was determined. In order to compare the reaction rates, the reaction with the primary alcohols was carried out in the range of 25-55°C, while for the alcohol containing the secondary hydroxyl group and DEGME the reaction was carried out in the range of 45-75°C. Based on the apparent activation energy values, it was found that the reactivity of 4,4'-MDI and 2,4-TDI to alcohols decreases with decreasing nucleophilicity of the alcohols in the order of butan-1-ol > butan-2-ol > DEGME.

1.3. We established that the reactivity of the investigated polymer diols decreases in the following order: PCLD> PTHF> PPG. We also showed that under the reaction conditions we used, the two hydroxyl groups reacted with the diisocyanate, no allophanate formation took place. The reactivity of the hydroxyl groups of different polyols towards isocyanate groups was determined. We have shown that MALDI-TOF MS is a suitable method to study the kinetics of the reaction of 4,4'-MDI with different polymeric polyols. Using MALDI-TOF MS, the response factors and intensities, the molar fractions of the polymer series were determined, and then the pseudo first-order rate constants were estimated by fitting. **Figure 3** reveals the MALDI-TOF MS spectra of the quenched reaction mixture obtained in the reaction of PPG with MDI at 3 different reaction times

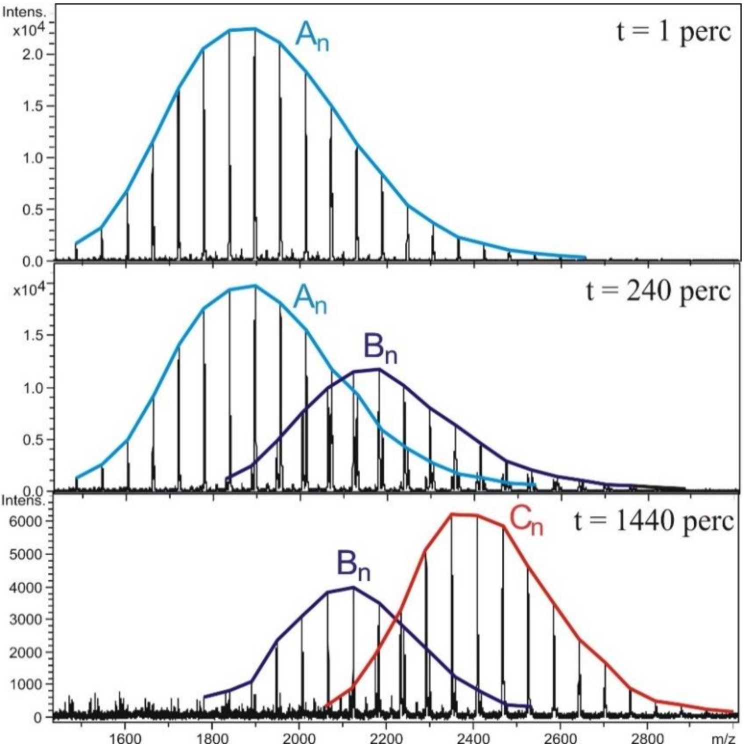

Figure 3. MALDI-TOF MS spectra of the quenched reaction mixture obtained in the reaction of PPG with MDI at 3 different reaction times

1.4. The substitution effect of polyols was identified. For the 4,4’-MDI - polymer triol (PPG_GL) system, we also estimated the pseudo first-order rate constants k_1, k_2 and k_3 by fitting. We found that after the first hydroxyl group of PPG_GL reacted, the second proceeds faster with the isocyanate group, indicating a positive substitution effect. The extent of the substitution effect was also determined graphically. Plotting the molar fractions of the products formed in the reactions as a function of the molar fraction of the starting reactant, it was shown that there is no substitution effect in the case of diols, while in the case of the polymer triol the substitution changes the reactivity of the remaining hydroxyl groups. **Figure 4** shows the change in the molar fraction [X_{Bn} (a) and X_{Cn} (b)] of the products formed in the 4,4'-MDI - PPG_GL reaction as a function of X_{An}.

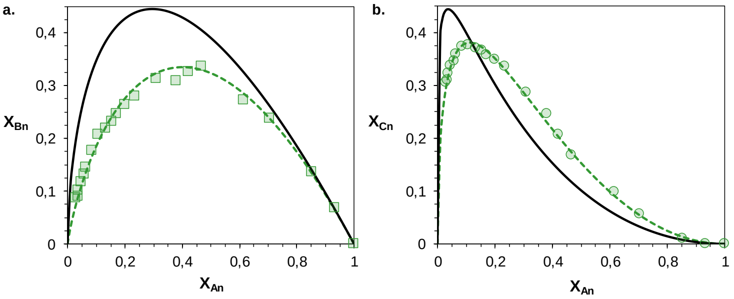

Figure 4. Variation of $\boldsymbol{X_{B_n}}$ (a) and $\boldsymbol{X_{C_n}}$ (b) as a function of $\boldsymbol{X_{A_n}}$ for PPG_GL. The solid lines show the theoretical curves for the cases of no substitution effect, while the dotted lines represent the best fitting.

2. Use of DART ion source for the identification and detection of chemical residues in textiles.

2.1. We pointed out that DART-MS can effectively detect quinoline and its methylated derivatives, phthalate-type plasticizers, amines, caprolaktam and ethoxylated fatty alcohols in garments. From the surfaces of 15 textile products, 40 different compounds were identified by DART-MS. Tandem (DART-MS / MS) mass spectrometry was performed on 14 of these compounds and their structures were proposed. In **Figure 5**, there is “Sample No 12. socks" DART-MS spectrum, showing the identified components with their structure and *m/z*.

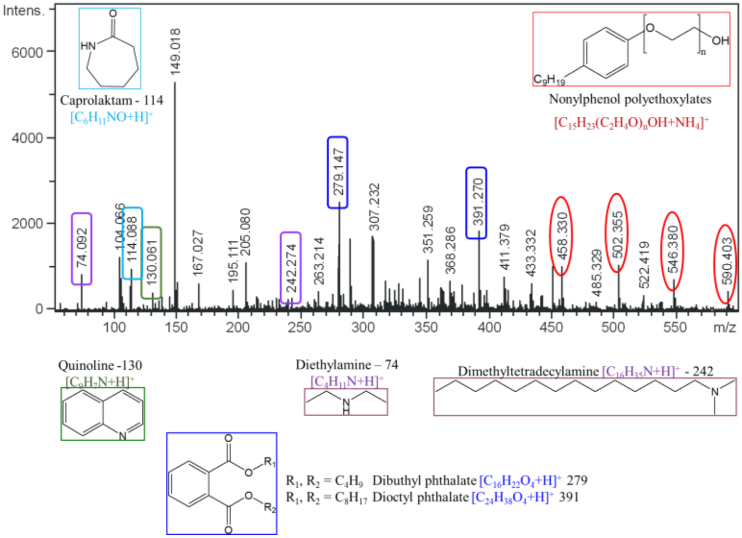

Figure 5. DART-MS spectrum of “Sample No 12. socks" and the identified components with their structure and *m/z*

2.2. We established that several textile article contained nonylphenyl ethoxylate, and their structure was confirmed by tandem mass spectrometry. We detected the presence of toxic nonylphenol ethoxylates (NPEs) in 8 samples, and we also detected members of the NPE series on the skin of a person wearing a textile item contaminated with NPE residues. Based on these findings, we found that nonylphenol ethoxylate components can be detected with high efficiency by DART ionization.

2.3. We developed an automated method for the detection of nonylphenyl ethoxylate components using tandem mass spectrometry. The measurement and evaluation time was reduced to less than one minute per sample. The DART-MS spectrum of a “clean” sampling swab is presented in **Figure 6**. Red indicates adduct ions formed with ammonium ion, while blue indicates protonated adducts. Furthermore, for both series, the number of repeating ethylene oxide units is included.

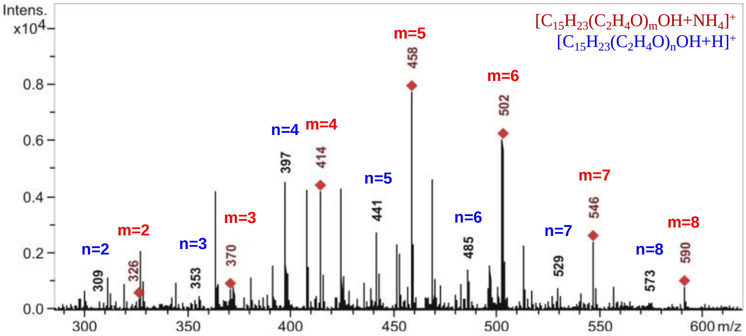

Figure 6. A DART MS spectrum of a swab. Red indicates adduct ions formed with ammonium ion, while blue indicates protonated adducts. Furthermore, for both series, the number of repeating ethylene oxide units is included.

IV Possible application of the results

We have demonstrated that the soft ionization techniques we used, such as ESI-MS and MALDI-TOF MS, are fast and efficient methods for the kinetic studies of the reaction of diisocyanates with alcohols and polymer polyols. Based on our measurements, these MS methods allow the progress of the reactions of compounds with similar properties and monitoring the distribution of the reaction products. Furthermore, using the time-independent diagrams, information on the substitution effect can also be obtained. The so determined pseudo first-order rate constants and substitution effects can be used for the design of product properties.

We proved that the DART-MS method can be applied for the analysis of different clothing items as a non-destructive technique. Based on the results further products and items can be involved in a similar research topic. The identified nonylphenol-ethoxylate components and the identification of other irritant and toxic compounds help in the monitoring of such molecules.

Acknowledgement

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V Publication List

List of publications related to the dissertation

1. **Antal, B**.; Kuki, A.; Nagy, L.; Nagy, T.; Zsuga, M.; Keki, S. Rapid detection of hazardous chemicals in textiles by direct analysis in real-time mass spectrometry (DART-MS). *Anal. Bioanal. Chem.* **2016,** 408 (19), 5189-5198. IF: 3,431

2. Nagy, T.; **Antal, B**.; Czifrak, K.; Papp, I.; Karger-Kocsis, J.; Zsuga, M.; Keki, S. New insight into the kinetics of diisocyanate-alcohol reactions by high-performance liquid chromatography and mass spectrometry. *J. Appl. Polym. Sci.* **2015,** 132 (25). IF: 1,866

3. Nagy, T.; **Antal, B.**; Dekany-Adamoczky, A.; Karger-Kocsis, J.; Zsuga, M.; Keki, S. Uncatalyzed reactions of 4,4 '-diphenylmethane-diisocyanate with polymer polyols as revealed by matrix-assisted laser desorption/ionization mass spectrometry. *Rsc Advances* **2016,** 6 (52), 47023-47032. IF: 3,108

List of other publications

4. Kuki, Á.; Shemirani, G.; Nagy, L.; **Antal, B.**; Zsuga, M.; Kéki, S. Estimation of Activation Energy from the Survival Yields: Fragmentation Study of Leucine Enkephalin and Polyethers by Tandem Mass Spectrometry. J. Am. Soc. Mass. Spectrom. 2013, 24 (7), 1064-1071. IF:3,193

5. Kuki, Á.; Nagy, L.; Szabó, K. E.; **Antal, B**.; Zsuga, M.; Kéki, S. Activation Energies of Fragmentations of Disaccharides by Tandem Mass Spectrometry. J. Am. Soc. Mass. Spectrom. 2014, 25 (3), 439-443. IF: 2,945

6. Nagy, L.; Nagy, T.; Deak, G.; Kuki, A.; **Antal, B.**; Zsuga, M.; Keki, S. Direct analysis in real time mass spectrometry (DART-MS) of highly non-polar low molecular weight polyisobutylenes. J. Mass Spectrom. 2015, 50 (9), 1071-1078. IF: 2,541

7. Nagy, T.; Kuki, A.; **Antal, B.**; Nagy, L.; Purgel, M.; Sipos, A.; Nagy, M.; Zsuga, M.; Keki, S. Chiral differentiation of the noscapine and hydrastine stereoisomers by electrospray ionization tandem mass spectrometry. J. Mass Spectrom. 2015, 50 (1), 240-246. IF: 2,541

8. **Antal, B.**; Kuki, A.; Nagy, L.; Nagy, T.; Zsuga, M.; M-Hamvas, M.; Vasas, G.; Keki, S. Rapid Discrimination of Closely Related Seed Herbs (Cumin, Caraway, and Fennel) by Direct Analysis in Real Time Mass Spectrometry (DART-MS). Anal. Sci. 2016, 32 (10), 1111-1116. IF: 1,228

Conferences

9. **Antal, B**.; Kuki, Á.; Shemirani, G.; Nagy, L.; Zsuga, M.; Kéki, S., Poliéterek és a diizodecil-ftalát fragmentáció aktiválási energiájának becslése tandem tömegspektrometria segítségével. In XIX. Nemzetközi Vegyészkonferencia, Nagybánya, Románia, 2013.

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11. **Antal, B**.; Kuki, Á.; Nagy, L.; Nagy, T.; Zsuga, M.; Kéki, S., A római kömény, a fűszerkömény és az édeskömény gyors elemzése valós idejű közvetlen analízis alkalmazásával. In XXI. Nemzetközi Vegyészkonferencia, Csíksomlyó, Románia, 2015.

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14. **Antal, B**.; Nagy, T.; Dékány-Adamóczky, A.; Karger-Kocsis, J.; Zsuga, M.; Kéki, S., Matrix-Assisted Laser Desorption Ionization mass spectrometric study of 4, 4'-diphenyl-methane-diisocyanate and polyols uncatalyzed reactions. In 20th European Symposium on Polymer Spectroscopy, Dresden, Germany, 2016.

15. Kuki, Á.; **Antal, B.**; Nagy, L.; Nagy, T.; Zsuga, M.; Kéki, S., Vegyi anyagok gyors detektálása ruhadarabokon valós idejű közvetlen analízis ionizációs tömegspektrometriával (DART-MS). In XXII. Nemzetközi Vegyészkonferencia, Temesvár, Románia, 2016.

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17. Kuki, Á.; **Antal, B**.; Nagy, L.; Nagy, T.; Zelei, G.; Zsuga, M.; Kéki, S., Identification of chemicals in different objects by direct analysis in real time mass spectrometry. In XXII. International Mass Spectrometry Conference, Florence, Italy, 2018.

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Doctoral School: Doctoral School of Chemistry

List of publications related to the dissertation

Foreign language scientific articles in international journals (3)

1. **Antal, B.**, Kuki, Á., Nagy, L., Nagy, T., Zsuga, M., Kéki, S.: Rapid detection of hazardous chemicals in textiles by direct analysis in real-time mass spectrometry (DART-MS).
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List of other publications

Foreign language scientific articles in international journals (5)

4. **Antal, B.**, Kuki, Á., Nagy, L., Nagy, T., Zsuga, M., Mikóné Hamvas, M., Vasas, G., Kéki, S.: Rapid Discrimination of Closely Related Seed Herbs (Cumin, Caraway, and Fennel) by Direct Analysis in Real Time Mass Spectrometry (DART-MS).
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   IF: 3.193

Total IF of journals (all publications): 20,853
Total IF of journals (publications related to the dissertation): 8,405

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