Acid digestion of nonwoven textiles for measuring their trace element content by ICP techniques

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Method Article

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Abstract

We present herein a digestion method based on high-temperature (260 °C) microwave heating and strong acidic media in order to perform a complete digestion of nonwoven textiles, which can be found in face masks. In particular, this protocol allows the digestion of PET-, PTFE-, polyamide- and elastane-containing textiles resulting in a complete release of metallic contents in order to analyze their elemental contents by ICP techniques.

Introduction

Nonwovens textiles are a type of textiles in which the fabric is produced directly by bonding a mass of fibers together using physical (i.e. heat, pressure) or chemical (binding agent) means[1,2]. They differentiate from conventional woven textiles in that the weaving and knitting process is omitted. Any compound able to form fibers may be used to form a nonwoven textile. The most common fiber materials used are cotton, wood pulp and rayon fibers for cellulose-based materials and polypropylene (PP), polyethylene terephthalate (PET) and nylon for man-made fibers[2]. Binders and additives are other raw materials that are used in the production of nonwoven textiles. Binders such as starch, glue, casein, rubber, latex, cellulose derivatives and synthetic resins are adhesives for fiber bonding, whereas additives like pigments and fillers are used to provide special aesthetical and functional properties to the textiles[3].

As a result, textiles can contain metal contaminants and other impurities that come from the raw materials used during the manufacturing process[4]. For example, metals such as vanadium, chromium, barium, lead, copper, cobalt and nickel can be found in dyes used to color textiles, while antimony is used as a catalyst in PET manufacture[4]. Additionally, textiles can be functionalized with micro- and nanoparticles of various natures depending on their intended use and design[5,6]. Nanoparticles of titanium dioxide (TiO_2) and zinc oxide (ZnO) are commonly used as UV-blockers, nano-silica (SiO_2) can be used to improve wrinkle resistance of silk, nanosilver (Ag) and copper (Cu) (and copper oxide, CuO) nanoparticles are used for antibacterial properties and nanoantimony doped tin dioxide (Sb-SnO_2) is used to provide antistatic properties[4,7,8]. Among these particles, TiO_2 particles are also used to reduce UV fatigue of the materials, create antimicrobial filters, enhance self-cleaning and as a bleaching or matting agent[9,10,11,12]. Such clothing technologies are used in personal protective equipment (PPE) and, as a result, can be found in face masks, which have been recommended as a health measure to protect from covid-19. A recent publication revealed that about 70% of tested batches of face masks intended to be put on sale as personal protective equipment, contained TiO_2 in amounts up to 2000 mg kg^{-1} [13]. Indeed, the work by Verleysen et al. 2022, which used the present protocol, corroborated the presence of TiO_2 particles in face masks made of synthetic textile fibers, in levels ranging from 0.8 to 152 mg TiO_2 per mask[14].

Since textiles interact directly with the skin or can be in close contact with the mouth and the nose as in the case of face masks, the presence of potentially toxic elements or particles may present a safety risk

when absorbed or inhaled. For instance, recent studies reported toxic effects in animals after TiO_2 particle inhalation[15] or ingestion[16] and thus raise a concern about human health due to large face mask utilization as a public health measure since the beginning of covid-19 crisis[17]. Hence, determination of the concentration of trace elements in nonwoven textiles is necessary to assess exposure. Common analytical techniques used for element quantification (i.e. ICP-OES, ICP-MS) require that the samples are present as a homogeneous solution. A way to achieve this is through sample digestion. The wide variety of materials used in nonwoven textiles makes it difficult to digest them following conventional procedures. Residues and turbidities can be observed in solution after digestion[4], especially among the nonwoven textiles where materials such as PET, PTFE, polyamide and elastane are used[2]. Hydrophobic textiles can be encountered as well, leading to possible clog of the ICP nebulizer[18]. As a result, a new digestion protocol is required for such nonwoven textiles. Such a procedure was developed for microwave digestion as this method is efficient and shows good performance in comparison with other methods[19,20]. In this protocol, we introduced a technical novelty which consists in performing first a charring step before the digestion step.

Reagents

- Sulfuric acid (H_2SO_4) 93-98% (CARLO ERBA, CAS: 7664-93-9, E.E.C. n°231-639-5, 2.5 L)
- Nitric acid (HNO_3) 67-69% (CARLO ERBA, CAS: 7697-714-2, E.E.C. n°231-714-2, 2.5 L)
- De-ionized (DI) water (double distilled, 1.0 - 1.5 µS cm^{-1}, 0.7-1.0 mOhm x cm)

Equipment

- Scissors
- Variable volume pipette 1-10 mL (Eppendorf Research Plus, Ref: 3123000080)
- Micropipette tips 10 mL (Eppendorf; Ref: 0030071654)
- 50 mL graduated polypropylene screw cap tubes (Sarstedt, Ref: 62.559.001)
- Weighing scale (SARTORIUS, Germany)
- iPrep 110 mL PTFE vessels and caps (CEM; USA)
- Mars 6 microwave (CEM; USA)

Procedure

Sample preparation

1. Use scissors to remove any non-textile parts and to cut the textile into square pieces of approximately 5x5 mm^2. For blank samples containing no textile sample, directly start at step 4.

2. Manually mix the textile square pieces to obtain a homogeneous sample.

3. Weigh out 200 ± 10 mg of the sample in a weighing boat, note the weight and transfer it into the iPrep vessels ensuring that all pieces remain at the bottom of the vessel. Otherwise, gently tick on the tube.

Charring step

4. Add 6 mL of concentrated H_2SO_4 to the iPrep vessels using a pipette. Ensure that all the sample pieces are in contact with the acid.

5. Leave the sample to pre-digest for 15 minutes with the cap covering the tube to avoid contamination but untightened in order to allow overpressure release.

6. Close the iPrep vessel and insert it into the microwave oven with a limit of 4 samples per run. All the samples should be of similar material for safety reasons. It is recommended that blanks (no textile) and samples are not digested in the same run.

7. Heat the samples up to 260 °C using a single 30 minutes stage “ramp-to-temperature” option with 900W power max and 100% power. Hold for 5 minutes at this temperature. Thereafter, allow to cool down below 60 °C.

Digestion step

8. Once tube temperature is below 60 °C, carefully open the vessel under fume-hood and gently add 10 mL of HNO_3 using a pipette.

9. Leave the sample to pre-digest for 30 minutes under fume-hood with the cap covering the tube to avoid contamination but untightened in order to allow pressure evacuation.

10. Close the iPrep vessel and insert it into the microwave oven.

11. Heat the samples up to 200 °C using a single 30 minutes stage “ramp-to-temperature” option with 900W power max and 100% power. Hold for 10 minutes at this temperature. Thereafter, allow to cool down below 60 °C.

Conditioning

12. Carefully open the vessel under the fume-hood to evacuate toxic fumes. Pour the liquid into a 50 ml Sarstedt vessel.

13. Rinse the iPrep vessel with a few mL of DI water and carefully add the rinsing waters into the Sarstedt vessel. Repeat two more times.

14. Add DI water to the Sarstedt vessel up to the 50 mL volume mark and manually agitate the sample to homogenize the solution.

15. Diluted samples are refrigerated until analysis by ICP-OES or ICP-MS.

Troubleshooting

- Steps: 4-5; 8-9

Problem: fumes or violent reactions are observed.

Possible reason: the samples contain highly reactive materials.

Solution: work under fume hood with adequate safety equipment / consider softer alternative such as diluted acids / consider to weigh less material for digestion.

- Steps: 7-8; 11-12

Problem: overpressure observed inside the vessel.

Possible reason: digestion of fibers has formed gases such as CO_2.

Solution: work under fume hood with adequate safety equipment / carefully open the venting hole / consider to weigh less material for digestion.

- Steps: 7, 11

Problem: error in microwave program.

Possible reason: different reactivity of materials in same run.

Solution: run only comparable materials in one run.

- Step: 12

Problem: large amount of gas inside the vessel.

Possible reason: degradation of nitric acid has generated NO_x toxic gases.

Solution: carefully open the venting hole under fume hood with high air flux.

- Step: 13

Problem: fumes or violent reactions are observed.

Possible reason: the addition of water to strong acids generates an exothermic reaction.

Solution: work under fume hood with adequate safety equipment, add the rinsing waters carefully.

- Step: 14

Problem: abnormal/ erratic signals are obtained after analysis.

Possible reason: the microwave vessels are contaminated by previous experiments.

Solution: clean the microwave vessels (using 10 ml pure HNO_3, 6 ml pure H_2SO_4 and run the Easy Prep clean[21] program) and redo the experiment.

Time Taken

The whole procedure is expected to last for about 3 hours, which can be divided into the four following stages:

- Sample preparation (steps 1-3): 40 min
- Charring step (steps 4-7): 45 min
- Digestion step (steps 8-11): 85 min
- Conditioning (steps 12-15): 10 min

Anticipated Results

The expected outcome of the procedure is 50 mL of perfectly clear (no visible particles) yellowish solution, suitable for analysis.

References

1. Chua, M. H. *et al.* Face Masks in the New COVID-19 Normal: Materials, Testing, and Perspectives. *Research* **2020**, 1–40 (2020).

2. T. Karthik, Prabha Karan C., & R. Rathinamoorthy. *Nonwovens: Process, Structure, Properties and Applications*. (Woodhead Publishing India PVT. Limited, New-Delhi, India, 2017). doi:10.1201/9781315365022.

3. *Complete Textile Glossary*. (Celanese Acetate LLC, New-York, USA, 2001).

4. Rujido-Santos, I., Herbello-Hermelo, P., Barciela-Alonso, M. C., Bermejo-Barrera, P. & Moreda-Piñeiro, A. Metal Content in Textile and (Nano)Textile Products. *IJERPH* **19**, 944 (2022).

5. Palmieri, V., De Maio, F., De Spirito, M. & Papi, M. Face masks and nanotechnology: Keep the blue side up. *Nano Today* **37**, 101077 (2021).

6. Valdiglesias, V. & Laffon, B. The impact of nanotechnology in the current universal COVID-19 crisis. Let's not forget nanosafety! *Nanotoxicology* **14**, 1013–1016 (2020).

7. Saito, M. Antibacterial, Deodorizing, and UV Absorbing Materials Obtained with Zinc Oxide (ZnO) Coated Fabrics. *Journal of Coated Fabrics* **23**, 150–164 (1993).

8. Staneva, D., Atanasova, D., Nenova, A., Vasileva-Tonkova, E. & Grabchev, I. Cotton Fabric Modified with a PAMAM Dendrimer with Encapsulated Copper Nanoparticles: Antimicrobial Activity. *Materials* **14**, 7832 (2021).

9. Windler, L. *et al.* Release of Titanium Dioxide from Textiles during Washing. *Environ. Sci. Technol.* **46**, 8181–8188 (2012).

10. Karbownik, I., Kowalczyk, D., Malinowska, G. & Paruch, B. Antibacterial Properties of Polyester Fibres' Materials with Titanium Dioxide Deposited on Their Surface. *Acta Phys. Pol. A* **116**, S-169-S-171 (2009).

11. Gao, C. *et al.* Continuous dry–wet spinning of white, stretchable, and conductive fibers of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and ATO@TiO2 nanoparticles for wearable e-textiles. *J. Mater. Chem. C* **8**, 8362–8367 (2020).

12. Aalipourmohammadi, M., Davodiroknabadi, A. & Nazari, A. Homogeneous Coatings of Titanium Dioxide Nanoparticles on Corona-Treated Cotton Fabric for Enhanced Self-Cleaning and Antibacterial Properties. *Autex Research Journal* **21**, 101–107 (2021).

13. Piernicola Pedicini, Rosa D'Amato, Eleonora Evi, & Ignazio Corrao. Titanium dioxide in personal protective equipment (PPE). https://www.europarl.europa.eu/doceo/document/E-9-2020-005899_EN.html.

14. Verleysen, E. *et al.* Titanium dioxide particles frequently present in face masks intended for general use require regulatory control. *Sci Rep* **12**, 2529 (2022).

15. Bermudez, E. *et al.* Pulmonary Responses of Mice, Rats, and Hamsters to Subchronic Inhalation of Ultrafine Titanium Dioxide Particles. *Toxicological Sciences* **77**, 347–357 (2004).

16. Bettini, S. *et al.* Food-grade TiO2 impairs intestinal and systemic immune homeostasis, initiates preneoplastic lesions and promotes aberrant crypt development in the rat colon. *Sci Rep* **7**, 40373 (2017).

17. Peeples, L. WHAT THE DATA SAY ABOUT WEARING FACE MASKS. *Nature* **586**, 186–189 (2020).

18. Rezić, I., Zeiner, M. & Steffan, I. Determination of 28 selected elements in textiles by axially viewed inductively coupled plasma optical emission spectrometry. *Talanta* **83**, 865–871 (2011).

19. Mara, A. *et al.* Multi-Elemental Analysis as a Tool to Ascertain the Safety and the Origin of Beehive Products: Development, Validation, and Application of an ICP-MS Method on Four Unifloral Honeys Produced in Sardinia, Italy. *Molecules* **27**, 2009 (2022).

20. Tuzen, M., Onal, A. & Soylak, M. Determination of trace heavy metals in some textile products produced in Turkey. *Bull. Chem. Soc. Eth.* **22**, (2008).

21. *iPrep High Performance Vessels Manual*. (CEM Corporation, Matthews, NC, USA, 2019).

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Supplementary Files

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- Aciddigestionofnonwoventextilesformeasuringtheirtraceelementcontentby ICPtechniques.docx