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Analysis and detection of homemade explosive TACP

Robert Matyáš[1], Zdeněk Jalový[1], Ondřej Vodochodský[1*], Zuzana Zmrhalová[2], Jaroslav Maixner[3], Ladislav Lapčák[3], Petr Baroš[4], Jiří Hausner[5], Pavel Kolba[6], Zuzana Čapková[7]

[1] Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 95, 53210, Pardubice, Czech Republic
[2] Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Studentska 95, 53210 Pardubice, Czech Republic
[3] Central Laboratories, University of Chemistry and Technology Prague, Technicka 5, 16628, Prague, Czech Republic
[4] Department of Sustainable Fuels and Green Chemistry, Faculty of Environmental Technology, University of Chemistry and Technology Prague, Technicka 5, 16628, Prague, Czech Republic
[5] Institute of Criminalistics, Police of the Czech Republic, Strojnicka 27, p.o. box: 62/KÚ, 17089 Praha 7, Czech Republic
[6] Directorate of Foreign Police, Inspectorate of Foreign Police, International Airport Prague – Ruzyně, Czech Republic
[7] Canine Behavior Research Center, Department of Animal Science and Ethology, Czech University of LifeSciences Prague, Prague 6, Czech Republic

[*]Corresponding author: ondrej.vodochodsky@upce.cz

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Abstract:

This paper focuses on tetraamminecopper(II) perchlorate (TACP), a relatively newly used and popular homemade explosive that is insufficiently described in the literature. The compound was analyzed using commonly used forensic laboratory techniques such as FTIR, Raman, XRPD, and DTA. The TACP molecule was labeled with four ^{15}N atoms on ammonia ligands to assign vibrational modes to the resulting bands. The paper also describes the thermal decomposition of TACP using thermoanalytical methods TGA/MS. The TACP decomposes to the final product CuO in six distinct ranges, releasing N_2O, NO, HCl, O_2, H_2O, and NH_3. It has been discovered that TACP is not a stable compound and will decompose spontaneously to ammonia, ammonium perchlorate, and basic copper perchlorate within a few months if exposed to air at room temperature. Residues of precursors have been detected in TACP prepared by four improvised preparation methods published on the Internet. These residues can be used to identify the precursor used in the preparation. The post-blast residues of TACP are of ordinary shape, but the use of TACP as an explosive can be indicated by the presence of a high content of copper and chlorine atoms in post-blast residues. The results of canine detection of TACP indicate that the dog is able to detect TACP, but the dog is likely to focus on the smell of ammonia in the TACP odor.

Keywords: Tetraamminecopper(II) perchlorate, TACP, forensic analysis, powder diffraction, FTIR, Raman spectroscopy

1 Introduction

The first and second decades of the 21st century have seen a sharp increase in the number of terrorist attacks using homemade explosives in the Western world. Different countries have taken different approaches to limit this increase to protect civilians from the consequences of terrorist bomb attacks. One of them is regulating legislation on the availability of key homemade explosive precursors for the public.

The European Union has issued two regulations in the last decade, regulation 98/2013 and 2019/1148 [1, 2]. Both regulations cover the availability of nitromethane (liquid explosive used as a component of fuels for airplane models) and precursors of homemade explosives, in particular strong oxidizers (ammonium nitrate, sodium and potassium chlorate and perchlorate, hydrogen peroxide), energetic fuels (aluminum and magnesium powder), and precursors for synthesis of homemade explosives (acetone, nitric and sulfuric acid, hexamine) [3-5]. Due to the limited availability of the mentioned precursors, many homemade explosives producers focused on less common explosives that can be made from unregulated precursors. In recent years, cupric coordination compounds have become very popular, in particular tetraamminecopper(II) nitrate (TACN) and tetraamminecopper(II) perchlorate (TACP).

TACN is a relatively well-known substance. Although it has never become a significant explosive, it is well described in the literature, primarily as an undesirable product of the reaction of ammonium nitrate with copper or copper alloys [6-9]. Also, as a shilovite mineral, TACN has recently been found in a guano deposit [10].

TACP, on the other hand, is only marginally mentioned in the literature. Generally, cupric perchlorate forms several cupric complexes with ammonia that differ in the number of ammonium ligands [11-13]. The most stable is the mentioned tetraamine complex $Cu(NH_3)_4(ClO_4)_2$, TACP. Due to the content of the oxidizer part (perchlorate anion) and fuel part (ammonia ligands) of molecule TACP has explosive properties and belongs among explosives like some other substances such as ammonium nitrate [14, 15], ammonium perchlorate [15-17], urea nitrate [18, 19] or urea hydrogen peroxide [20-22].

The explosive character of TACP was first described in the first half of the 20th century [23], while more detailed studies of explosive parameters have been published recently. Its sensitivity to impact and friction is on the level of sensitive secondary explosives (PETN) and its explosive parameters are slightly lower than TNT [24-26].

TACP can be prepared by a simple reaction of cupric perchlorate with aqueous ammonia. Unfortunately, the availability of cupric perchlorate is not regulated by EU regulations, which, together with the popularization on the Internet, is reflected in the popularity of these homemade explosives nowadays [27]. Several cases of this improvised explosive being found and seized by security forces have already been reported in Europe. For example, it has emerged in a case study in Sweden [28]. Therefore, the use of TACP as a homemade explosive can be expected to continue to grow in the future. Since TACP analytical data are described incompletely in literature, we focused on the TACP analysis and its interpretation, concentrating primarily on common analytical methods used in forensic laboratories, including post-blast analysis.

Cupric perchlorate is a relatively exotic chemical with specific applications (mentioned in scientific literature as a specific catalyst or oxidant [29-35]) without any use in households. Therefore, it can be bought just from specialized companies that sell chemicals.

However, buying cupric perchlorate via the Internet creates a digital footprint, which may discourage some makers of homemade TACP from buying it. Moreover, cupric perchlorate has no reasonable use in households, and its buying and possession are at least suspicious. The possible digital footprint and limited accessibility of cupric perchlorate lead some amateur chemists to search for alternative procedures for TACP preparation using more readily available precursors than cupric perchlorate. Thus, traces of the original precursors may remain in the final product, where they can be detected. Identifying these traces can link to used precursors that could help in a forensic investigation and provide evidence for the courts.

In recent years, a number of papers have been published focusing on the identification of precursors or their sources for the most common homemade explosives like TATP [36-40], HMTD [41, 42], ammonium nitrate [43-45], erythritol tetranitrate [46-48] or urea nitrate [49, 50]. Therefore, the part of the article also focuses on identifying copper precursors in the final TACP.

2 Experimental part

Caution: Tetraamminecopper(II) perchlorate is explosive sensitive to mechanical stimuli, electrostatic discharge and the action of higher temperatures. Safety precautions for handling of explosives must be followed.

2.1 General methods

Elemental analysis (C, H, N) was performed on the Vario MICRO Cube (Elementar) in CHNS mode. Calibration was performed with sulphanilamide. The sample weight for analysis was 1 mg. Chlorine was determined by combustion of the sample in a Schoeniger bottle followed by potentiometric titration with 0.01 M silver nitrate using a 905 Titrando automatic titrator (Metrohm, Switzerland).

The infrared spectra were collected using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Medison, USA) with an ATR single reflection diamond accessory GladiATR (PIKE, USA). Measurement parameters were the spectral region 4000–400 cm^{-1}, resolution 4 cm$^{-1,}$ and number of scans 64. For evaluation of chemical shifts between TACP and $^{15}N_4$ labeled TACP, the resolution 1 cm^{-1} and number of scans 128 were used. Determination of water content by FTIR was performed using a twelve-reflection zinc selenide HATR accessory (Thermo

Scientific, Medison, USA), resolution 4 cm$^{-1,}$ and number of scans 64 were applied. The procedure used was as follows: 400 mg (weighed with an accuracy of 0.1 mg) of the TACP sample was dissolved in *N,N′*-dimethylformamide (99.8%, Extra Dry over Molecular Sieve, Acrōs Organics) in the volume of 5 ml and immediately measured. The water content was determined at 3546 cm^{-1} by comparison of the measured TACP spectrum with the spectra of *N,N′*-dimethylformamide containing the exact amount of water corresponding to the anticipated TACP hydrates. All spectral manipulations were made using Omnic 9.2 software.

The Raman spectra were acquired using a dispersive DXR Raman Microscope spectrometer (Thermo Scientific, Madison, USA). A diode-pumped Nd:YAG laser with a wavelength of 532 nm was employed as the excitation source. A grating with 900 lines/mm, 50 µm slit aperture, and 50x magnification objective were utilized, resulting in a spot size of approximately 1 µm in diameter. The measurements were conducted using a laser power of 0.3 mW, an integration time of 30 s, and 20 accumulations per spectrum.

The diffraction patterns were collected at room temperature with an Empyrean θ-θ powder diffractometer with parafocusing Bragg-Brentano geometry using Cu $K\alpha$ radiation (λ = 1.5418 Å, Ni filter, generator setting: 40 kV, 30 mA). An ultrafast *PIXcel*^{1D} detector with 255 channels was employed to collect XRD data over the angular range from 5 to 60 °2θ with a step size of 0.026° 2θ and a counting time of 0.04116 s/step.

Differential thermal analysis was carried out with a DTA 550 Ex thermal analyzer produced by OZM Research (Czech Republic). The samples were tested in glass micro test tubes in contact with air. The weight of samples was 10 mg and the heating rate was 5°C min^{-1}.

The simultaneous thermal analysis, which combines thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), was conducted using an STA 449 F5 Jupiter instrument (Netzsch, Selb, Germany). The gaseous products released during the TACP thermal decomposition were examined using a mass spectrometer (MS Clarus SQ 8T, PerkinElmer, USA). For the analysis, the sample was heated in an open alumina crucible from 30°C to 550°C at a heating rate of 5°C min^{-1} under a dynamic nitrogen atmosphere (20 ml min^{-1}; Linde N_2 4.6). The MS conditions were as follows: electron ionization (EI) at 70 eV and full scan mode (5 - 450 m/z). The data analysis was carried out using TurboMass™ GC/MS Software.

SEM images and energy-dispersive X-ray (EDX) analysis spectra of improvised prepared TACP were obtained using a scanning electron microscopy (Jeol JSM-5500LV, Japan) coupled with an energy-dispersive X-ray microanalyzer (detector GRESHAM Sirius 10). SEM images were taken in low vacuum mode and with the back-scattered electron detector.

Post-blast residues (PBR) from TACP detonation were analyzed according to the standardized protocol used by the Institute of Criminalistics - Police of the Czech Republic. PBR are firstly collected using carbon-coated adhesive targets for sampling of gunshot residues (company: LT Sezam s.r.o., Czech Republic, cat. No.: CH1010). The analysis is performed using SEM Tescan – MIRA 3 RISE (conditions: accelerating voltage 20kV, detector SE/BSE, WD 10 – 15 mm).

2.2 Syntheses

Ammonium perchlorate (Bochemie Plc. Bohumín), 24-29% aqueous solution of ammonia (Penta, p.a.), barium perchlorate (Aldrich, 97%), cupric carbonate basic (Fischer Chemicals, general purpose grade), cupric nitrate trihydrate (Lachner, p.a.), cupric oxide (Roth, ≥ 97.5%), cupric perchlorate hexahydrate (Acrōs Organics, 98%), cupric sulfate pentahydrate (Lachner, p.a.), (^{15}N)ammonium hydroxide solution (Sigma-Aldrich, ~ 14N solution in water, 98 atom % ^{15}N) were used as starting materials for syntheses.

2.2.1 Syntheses of Standards

Tetraamminecopper(II) perchlorate (TACP)

TACP was prepared by the reaction of cupric perchlorate hexahydrate with aqueous ammonia according to the literature [24], only the weights of reagents have been reduced twentyfold.

$$Cu(ClO_4)_2 \,.\, 6H_2O + 4NH_3 \longrightarrow [Cu(NH_3)_4](ClO_4)_2$$

The yield was 3.98 g (89.2% of theory). DTA: $T_{ign.}$ = 268°C (268°C [24]). Anal. Calc. for $H_{15}Cl_2CuN_4O_{9.5}$ (TACP·1.5 H_2O) (%): Cu, 17.77; H, 4.23; N, 15.67; Cl, 19.83. Found: Cu, 17.66; H, 4.11; N, 15.52; Cl, 20.05. FTIR and Raman spectra are reported in Table 1 in the Results and discussion section.

Tetra($^{15}N_4$)amminecopper(II) perchlorate (TACP-$^{15}N_4$)

Cupric perchlorate hexahydrate (373 mg, 1 mmol) was dissolved in 0.5 ml of water, and (^{15}N)ammonium hydroxide solution (0.9 ml, 16 mmol) was added. The mixture was stirred at room temperature for 15 min and then cooled to 0°C. The precipitate was filtered and dried at 50°C. The yield was 246 mg (73%). Anal. Calc. for $H_{12}Cl_2Cu^{15}N_4O_8$ (%): H, 3.62; Cu, 18.99. Found: H, 3.67; Cu, 18.89. DTA: $T_{ign.}$ = 266°C. FTIR and Raman spectra are reported in Table 1 in the Results and discussion section.

Basic cupric perchlorate, $Cu_4(ClO_4)(OH)_7 \cdot H_2O$

Cupric perchlorate hexahydrate (20.0 g, 54.0 mmol) was dissolved in 200 ml water, and sodium hydroxide (3.8 g, 95.0 mmol) in 25 ml water was gradually added at room temperature. The mixture was stirred for 1 hour, the solid formed was filtered, washed with water (3 x 50 ml), and finely with methanol. The precipitate was air-dried for 24 hours to give 5.4 g of fine blue powdered material (82%). DTA: 175°C (onset of endotherm 1), 194°C (onset of several multistep endotherm processes). Anal. Calc. for $Cu_4(ClO_4)(OH)_7{\cdot}H_2O$, $H_9ClCu_4O_{12}$ (%): H, 1.85; Cl, 7.22; Cu, 51.80. Found: H, 1.79; Cl, 7.40; Cu, 51.10. FTIR (cm^{-1}): 3610m (ν OH), 3590m (ν OH), 3559 (ν OH), 3520 (ν OH), 1627w (δ OH), 1496w, 1384w, 1109s ($\nu_{as.}ClO_4$), 1068s ($\nu_{as.}ClO_4$), 926w ($\nu_{s.}ClO_4$), 874m, 755m, 695m, 630m, 755m, 630m, 614sh (δClO_4), 602s, 502s, 459sh.

2.2.2 Improvised syntheses of TACP

TACP from cupric sulfate pentahydrate

Cupric sulfate pentahydrate was dissolved in water, and this solution was mixed with a stoichiometric amount of ammonium perchlorate dissolved in water. Then, the aqueous ammonia was added to this mixture in triple excess over stoichiometry. The precipitate was filtered and dried at room temperature. Other TACP samples were prepared using the same procedure, only ammonium perchlorate (in the form of aqueous solution with the same concentration) was used in excess of the stoichiometry (2x, 5x and 10x).

TACP from cupric oxide

Solid cupric oxide and a stoichiometric amount of solid ammonium perchlorate were placed in an Erlenmeyer flask. Then, the aqueous ammonia was added to this mixture in triple excess over stoichiometry, the mixture was briefly stirred and left at room temperature for 3h, 8h, 16h, 24h, or 72h, respectively. After the reaction time, the mixture was filtered, and the solid product was washed and left to dry at laboratory temperature.

TACP from basic cupric carbonate

Solid basic cupric carbonate and a stoichiometric amount of solid ammonium perchlorate were placed in an Erlenmeyer flask. An excess (3 times the stoichiometric amount) of aqueous ammonia was then added, the mixture was briefly stirred and left at room temperature for 3h, 8h, 16h, 24h, or 72h, respectively. After the reaction time, the mixture was filtered, and the solid product was washed and left to dry at laboratory temperature.

TACP from cupric sulfate and barium perchlorate

Cupric sulfate pentahydrate was dissolved in distilled water, this solution was then mixed with a stochiometric amount of barium perchlorate dissolved in distilled water. The mixture was allowed to decant, the white precipitate of barium sulfate was filtered off, and the blue cupric perchlorate solution was mixed with a triple excess of aqueous ammonia. The dark blue precipitate was filtered and left to dry at room temperature. In addition to the stoichiometric ratio of cupric sulfate to barium perchlorate, samples with a 10 and 20% excess of barium perchlorate and samples with a 10 and 20% deficiency of barium perchlorate were also prepared.

2.2.3 The treatment of TACP aged for 100 days in the open air

The aged TACP (0.703 g) was added into 5 ml methanol, stirred for 30 min at room temperature, and filtered. The solid was washed with methanol (5 x 5 ml) and air-dried to yield 0.239 g (35%) of a blue solid. DTA: 194°C (onset of several multistep endotherm processes). Anal. Calc. for $Cu_3(ClO_4)(OH)_5$, $H_5ClCu_3O_9$ (%): H, 1.34; Cl, 9.45; Cu, 50.82. Found: H, 1.51; Cl, 9.25; Cu, 50.15. FTIR: 91% spectral match with basic cupric perchlorate. Methanol from the filtrate was evaporated to give 0.459 g (65%) of bluish solid. Anal. Calc. for NH_4ClO_4, H_4ClNO_4: H, 3.43; Cl, 30.18; N, 11.92. Found: H, 3.31; Cl, 30.13; N, 10.90. FTIR: 98% spectral match with ammonium perchlorate.

2.3 Canine testing

For canine testing, TACP, ammonium perchlorate (TACP degradation product), and three other ammonium salts (chloride, sulfate, and carbonate) were used as target substances in quantities of 1-5 g. The TACP sample, which has limited chemical stability, was used only 1 week to 2 months after preparation. It was replaced by a fresh one after two months. The substances were placed in a sniffer (a small metal can with holes in the lid) and the sniffer was then placed in a 0.75 liter metal can. A total of 50 trials were performed for the target substance TACP and 25 trials for each of the other target substances. Various inorganic chemicals (but not ammonium salts) were used as distractors.

The detection tests were done with one canine not previously exposed to TACP. The canine was female Festival, a nine-year-old German Boxer trained seven years to alert to odors of the explosive compounds. The canine was trained by state police canine officer with more than 20 years of practice in explosive detection canine training. The positive reinforcement method was used to detect neat TACP. The training was done predominantly indoors under conditions similar to the final testing.

Testing was done over a six-month period with a two-week interval between testing days; the dog was routinely trained to detect common explosives and TACP among test days. The testing took place in the indoor premises of the Foreign Police at the Vaclav Havel International Airport Prague. The temperature during the tests was in the range from 19 to 21°C. Testing was carried out on line up of eight posts; one post with target chemicals, the other posts with distractors. During the testing, the canine handler entered the corridor with the line-up and, upon the command from an assistant, sent his canine off leash to the line-up. The canine went up along the metal cans, and when alerted, the assistant took note, and the canine handler left the room. The handler was not aware of the target odor position. The canine was rewarded when he found a TACP sample; in the case of other target odors (TACN and ammonium salts), he was not rewarded. The sequence of cans was changed after each trial.

The results of the tests with dogs were evaluated using the following parameters: Sensitivity for each target scent (percentage of correct responses) was calculated as the probability that a dog correctly indicates the target out of the total presentations of the target. Specificity was calculated as total correct rejections out of total posts across all trials. Accuracy represents the proportion of correctly classified results (the proportion of true results, either true positive or true negative).

This type of research has no impact on animal welfare because only non-experimental practices (in accordance with Act no. 166/1999 Sb. and Act no. 154/2000 Sb.) were used during the study. Only routine explosive detection training procedures were applied.

3 Results and discussion

3.1 Analyses of tetraamminecopper(II) perchlorate

3.1.1 Chemical analyses

The product after preparation was characterized by infrared and Raman spectroscopy, elemental analysis, and powder diffraction. The main groups in the molecule can be discovered using FTIR and Raman spectroscopies to confirm the compound structure.

To support infrared and Raman band assignment of the tetraamminecopper(II) perchlorate complex, labeled isotopologue ($^{15}N_4$)tetraamminecopper(II) perchlorate (TACP-$^{15}N_4$) was used for band assignment (Table 1). In this case, the specific $^{15}N_4$ labeling at four nitrogen atoms of ammonium ligands may distinguish between the bands influenced by the ammonia nitrogen represented by N–H stretching and deformation modes of ammonium ligands and Cu–N stretching vibrations. The bands that are not connected with the nitrogen atom are stretching vibrations and deformation of ClO_4^- anion and possible vibrations of OH groups. Thus, using selectively labeled TACP-$^{15}N_4$ with the use of spectral interpretation handbooks [51, 52] allows quite detailed band assignment and helps to prove the compound structure.

Table 1. Vibrational frequencies of tetraamminecopper(II) perchlorate (TACP) and tetra($^{15}N_4$)amminecopper(II) perchlorate (TACP-$^{15}N_4$)

FTIR [cm^{-1}]		Raman [cm^{-1}]		
TACP	TACP-($^{15}NH_3$)$_4$	TACP	TACP-($^{15}NH_3$)$_4$	Band assignment
3634vw	3634vw			rest of O–H
3568vw	3568vw			rest of O–H
3354m	3346m	3357m	3352m	ν(NH_3)
3286m	3282m	3287s	3283s	ν(NH_3)
3199m	3194m			ν(NH_3)
1615m	1612m			δ(NH_3)
1425w	1418w			δ(NH_4^+) from NH_4ClO_4
1252m	1247m			δ(NH_3)
1082sh	1082sh			$\nu_{as.}$(ClO_4)
1041s	1044s			$\nu_{as.}$(ClO_4)
932m	932m	933s	933s	$\nu_{s.}$(ClO_4)
915sh	915sh	915sh	915sh	$\nu_{s.}$(ClO_4)
685	682			δ(NH_3) *rock.*
616s	616s	626m	626m	δ(ClO_4)
459w	459w	462m	462m	δ(ClO_4)
433m	421m	431m	421m	ν(Cu–NH_3)
		312m	307m	ν(Cu–NH_3)

Abbreviations used: s – strong, m – medium, w – weak, vw – very weak (intensities), sh – shoulder, δ – deformation vibration, $\nu_{as.}$ - symmetric stretching, $\nu_{s.}$- symmetric stretching, *rock.* - rocking

The results of TACP analyses indicate that the material contains water as a hydrate. By FTIR, the water presence in the TACP molecule is easily evident in the solid state infrared spectrum by two medium to weak bands between 3400 and 3700 cm^{-1}. The content of water in TACP was determined quantitatively by dissolving it in anhydrous *N,N′*-dimethylformamide. The water amount was evaluated using the band of the free O–H bond vibration at 3546 cm^{-1}, which fits best the formula TACP·1.5 H_2O. The same content of water was proved by elemental analysis and weight loss of the sample dried in a desiccator. Placing TACP in a desiccator with calcium chloride, drying over 40°C, or even prolonged storage even in common room conditions leads to the loss of water molecules. Infrared spectra of anhydrous TACP show no band in the area 4000-3450 cm^{-1} and broad band at 533 cm^{-1} (Fig. 1). The weakly bound water in the molecule explains why some authors mention the water content of TACP [11, 12] and others do not [24-26, 53].

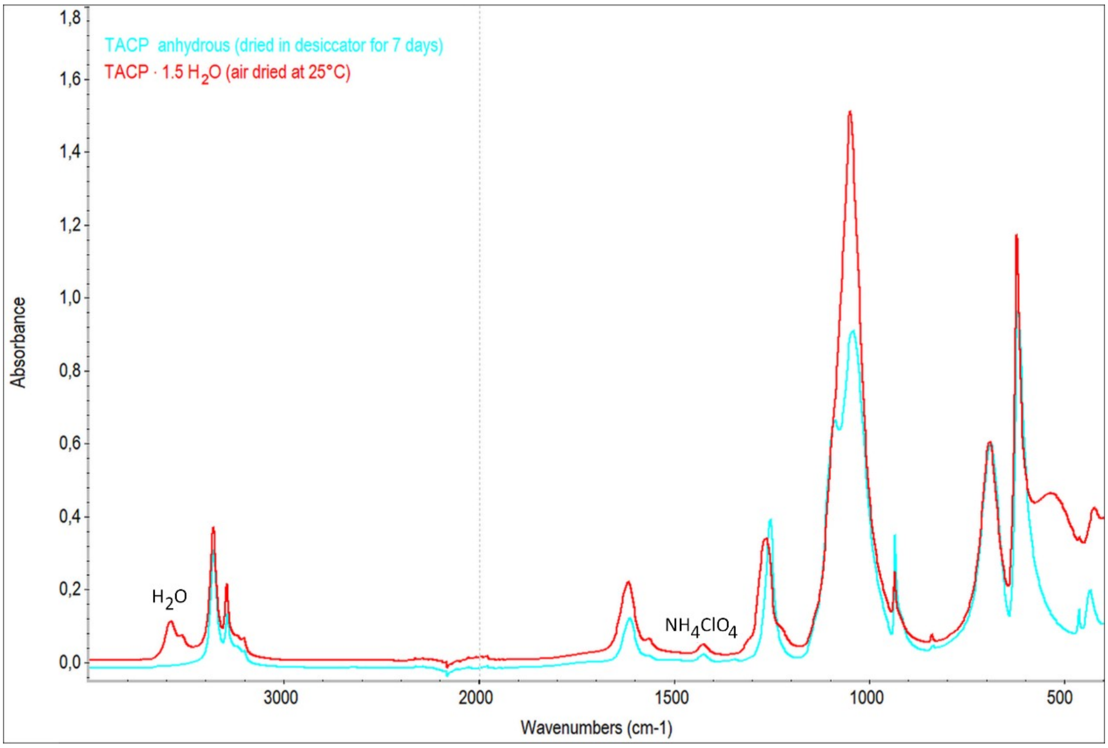

Fig. 1: Infrared spectra of TACP 1.5 hydrate and anhydrous TACP.

Another characteristic of TACP is that the product mostly contains traces of ammonium perchlorate as a by-product. The latter can be identified by FTIR using a band of weak to medium intensity at 1425 cm^{-1} (Fig. 1). Since ammonium perchlorate was not detected by XRPD in the TACP sample, its content is relatively low (maximum in the order of a few percent, concentration approximately 5% and above should be evident in X-ray powder diffraction pattern).

The XRPD diffraction analysis was used to determine the phase composition of TACP. The measured powder pattern is presented in Fig. 2 and contains reasonably sharp peaks. Therefore, the samples are crystalline with crystallites having regular 3D ordering of molecules and the size of coherent areas in the order of micrometers.

The software package HIGHSCORE PLUS V 3.0e (PANalytical, Almelo, Netherlands) [54] was used to smooth the data, to fit the background, to eliminate the $K\alpha_2$ component, and the top of the smoothed peaks were used to determine the peak positions, d-values, absolute and relative intensities of the diffraction peaks (Table 2). The d-values were calculated using Cu $K\alpha_1$ radiation (λ = 1.5406 Å).

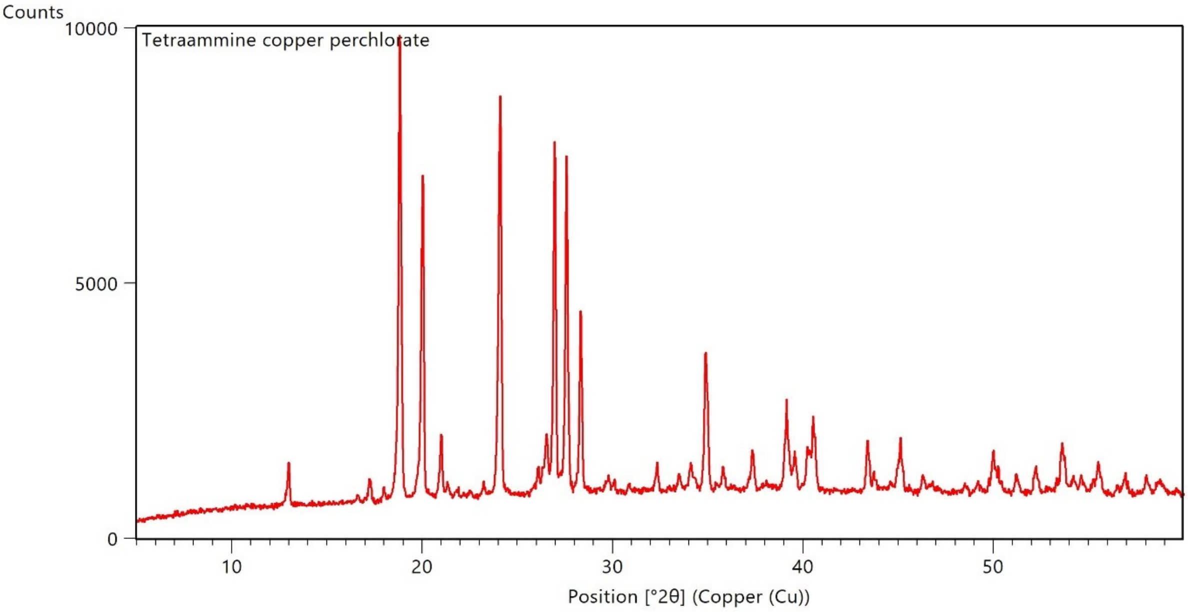

Fig. 2: X-ray powder diffraction pattern of tetraamminecopper(II) perchlorate using Cu$K\alpha$ radiation (λ = 1.5418 Å).

Table 2. X-ray powder diffraction data for $H_{12}N_6O_6Cu$. Only the peaks with I_{rel} of 10 or greater are presented. The d-values were calculated using Cu $K\alpha_1$ radiation (λ = 1.5406 Å).

$2\theta_{obs}$ (deg)	d_{obs} (Å)	I_{abs} (cts)	I_{rel} (%)
12,99	6,816	911	10
18,82	4,714	9392	100
20,02	4,435	6488	69
20,99	4,232	1274	14
24,09	3,695	7990	85
26,53	3,360	1206	13
26,95	3,308	7059	75
27,59	3,233	6792	72
28,33	3,151	3705	39
34,90	2,571	2809	30
39,13	2,302	1879	20
40,24	2,241	946	10
40,53	2,226	1554	17
43,39	2,085	1094	12
45,12	2,010	1158	12
49,99	1,825	901	10
53,60	1,708	1040	11

Search-match using d, I values was performed in the Powder Diffraction Files (PDF-4+ 2022, PDF-4 Organics 2022) [55] and in the Cambridge Structural Database (CSD, version 2023) [56]. A proper match was not found. Therefore, it can be concluded that there are no crystallographic data published for tetraamminecopper(II) perchlorate either in the PDF-4 databases or the CSD database.

Storage of TACP in air results in its chemical changes, generally in tens of days. The color of the material significantly changes from deep dark blue to bright blue. The changes can be successfully monitored by infrared and Raman spectroscopy, differential thermal analysis, and powder diffraction. A gradual increase of bands corresponding to ammonium perchlorate can be seen in the infrared spectra of TACP. Both infrared and Raman spectra of TACP stored for 100 days in open air highly correspond to ammonium perchlorate (Fig. 3, Fig. 4). In the case of elemental analyses, the most significant changes can be observed in the nitrogen content. From the initial 15.5% (of nitrogen found in the freshly prepared sample), the nitrogen content drops to 14.3% in three days, 12.3% in 19 days, and 7.9% in 50 days. The nitrogen content in 100 days old sample is 7.2%.

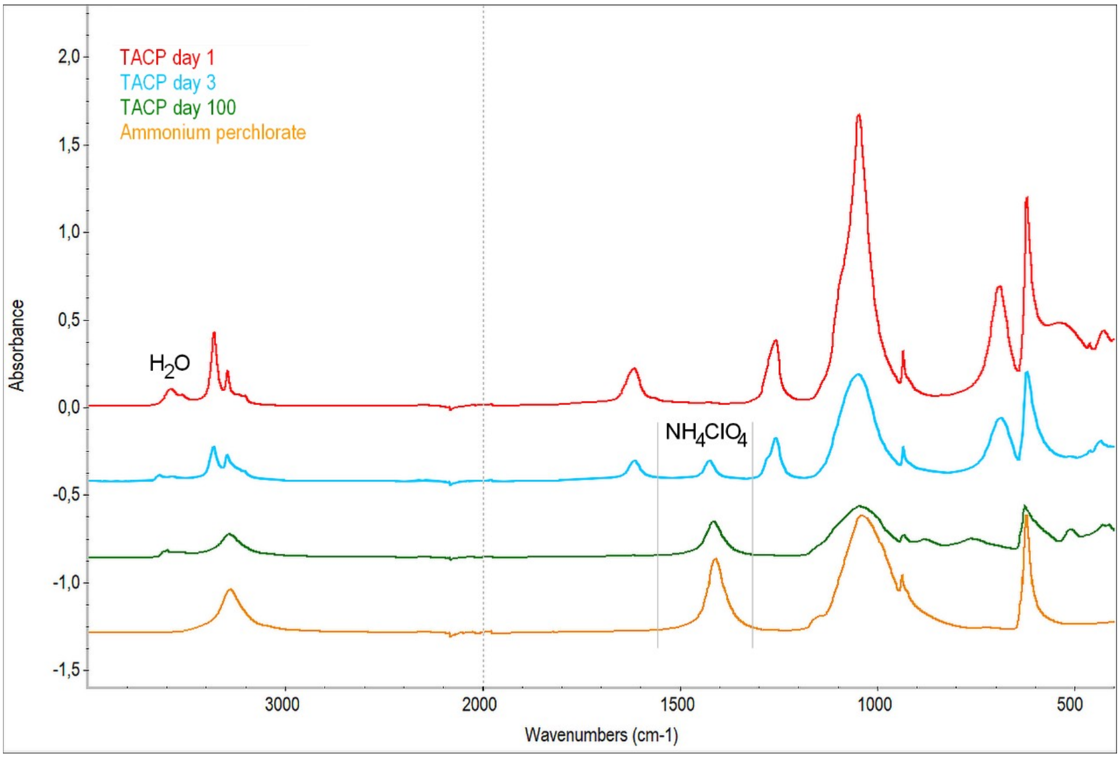

Fig. 3: Infrared spectra of TACP stored in open air for different times and comparison with ammonium perchlorate.

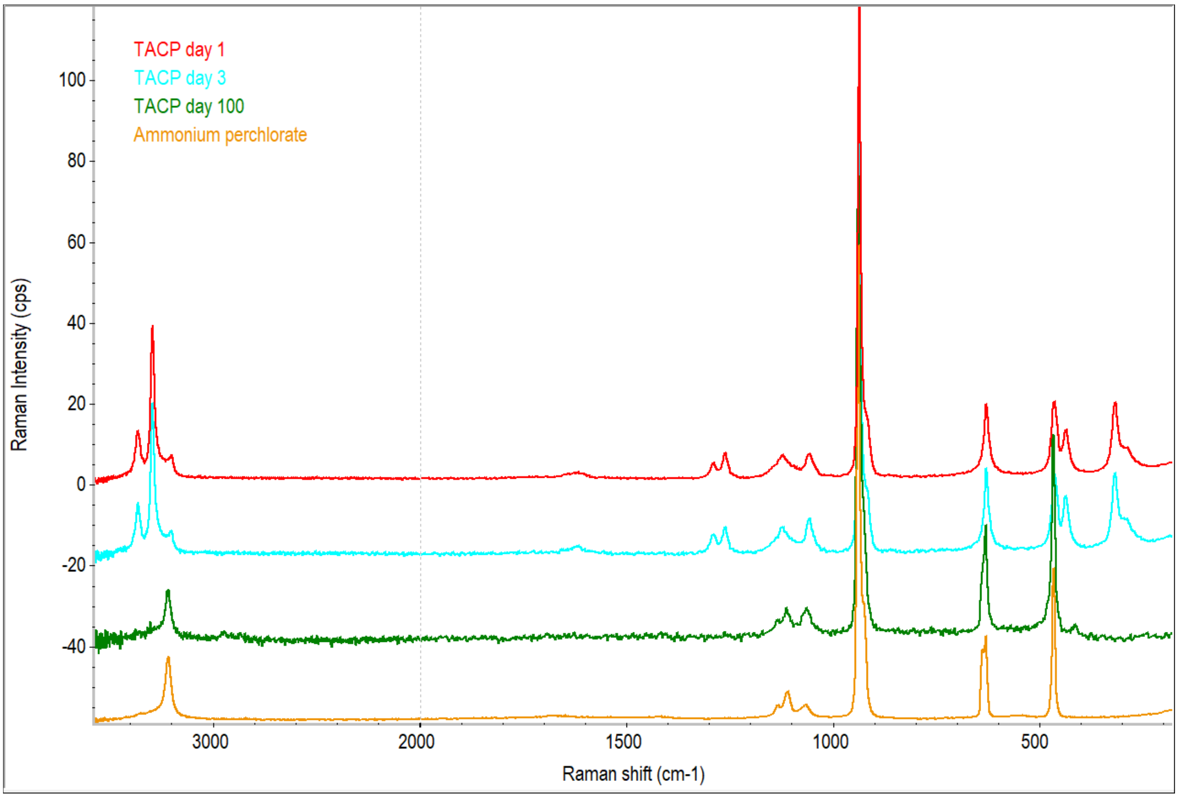

Fig. 4: Raman spectra of TACP stored in open air for different times and comparison with ammonium perchlorate.

The increasing content of ammonium perchlorate was also detected by XRPD. The three strongest peaks at 2θ=19.41°(I_{rel} (100%), d=4.571 Å), 2θ=22.71°(I_{rel} (45%), d=3.908 Å), especially 2θ=24.65°(I_{rel} (60%), d=3.609 Å) belonging to ammonium perchlorate are evident on the diffraction pattern (Fig. 5).

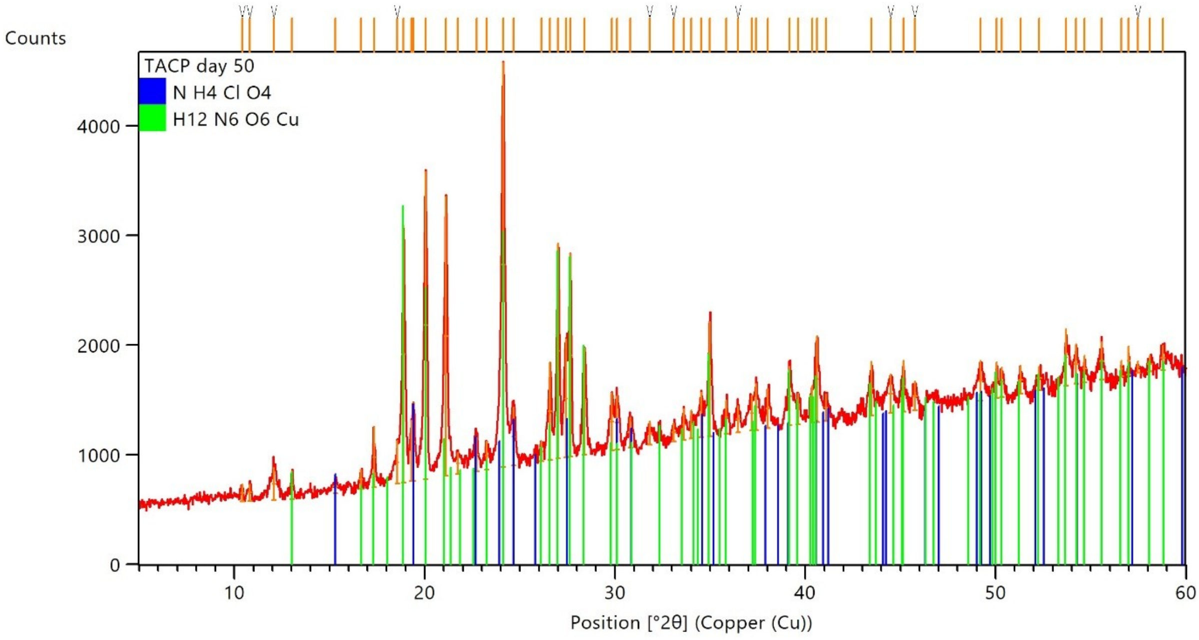

Fig. 5: X-ray powder diffraction pattern of TACP after 50 days stored in the open air using CuKα radiation (λ = 1.5418 Å).

In addition to the ammonium perchlorate and original TACP, the diffraction pattern contains several other peaks (2θ=12.05°, 32.33°, 35.92 and 44.44°) that indicate the presence of other compound. Its concentration in the TACP increases with storage time in the open air. After 100 days of storage, the material does not change further, and the final product contains ammonium perchlorate and mentioned other substances; the original TACP was not present in the material, even in a trace amount. A mixture of these two substances was separated by extraction with methanol, where ammonium perchlorate is well soluble. The content of ammonium perchlorate in 100-day-old material was thus determined to be 64% (ammonium perchlorate proved by FTIR and XRPD), and the content of insoluble residue was 36%. Based on elemental analysis, a chemical formula basic cupric perchlorate $Cu_3(ClO_4)(OH)_5$ was proposed for the second solid degradation product of TACP. Its infrared spectra and XRPD diffraction pattern (Fig. 6) show great agreement with the standard of basic cupric perchlorate prepared independently by the reaction of cupric perchlorate with sodium hydroxide, yielding a compound of the molecular formula $Cu_4(ClO_4)(OH)_7 \cdot H_2O$.

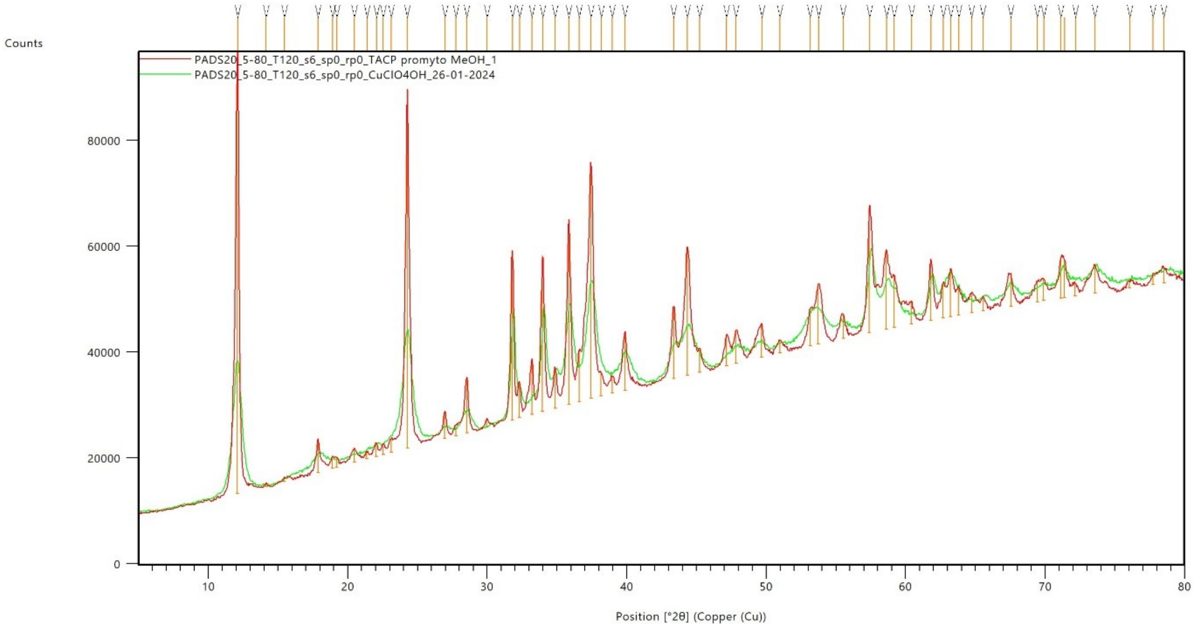

Fig. 6: X-ray powder diffraction pattern of solid degradation product of 100-days-old TACP sample after extraction of ammonium perchlorate (red record) compared to the basic cupric perchlorate standard (green record).

Taking into account the variety of basic cupric perchlorates [57-60], the result shows high agreement between the mentioned two samples. Based on the analyses performed, the degradation of TACP proceeds according to the following equation:

$$3\,[Cu(NH_3)_4](ClO_4)_2 + 5\,H_2O \longrightarrow 5\,NH_4ClO_4 + Cu_3(ClO_4)(OH)_5 + 7\,NH_3$$

The access to air strongly influences the degradation rate of TACP. The degradation is significantly reduced if the sample is stored in closed containers. Based on the FTIR spectrum, the TACP contains approximately 6% of ammonium perchlorate after 50 days of storage, 12% after 20 months, and 15% after three years of storage, for a sample stored in a polyethylene container with a plastic screw-on lid (without a sealing ring), at room temperature in a dark place.

3.1.2 Thermal analyses

In the case of substances that can be expected to be explosive, thermoanalytical methods, especially explosion-proof DTA, are commonly used in forensic laboratories. These analyses readily distinguish explosives from non-explosive substances by detecting highly exothermic decomposition typical for explosives. Moreover, the position of the peaks on the thermogram helps in the identification of explosives.

DTA thermogram of TACP contains an endo peak at 51°C, indicating the loss of crystal water. The storage of TACP in a desiccator, drying over 40°C, or prolonged storage even at common room conditions leads to loss of the crystal water, resulting in the absence of an endo peak at 51°C on the thermogram. The start of exothermic decomposition takes place at 207°C, resulting in ignition at 268°C. The ignition of 10 mg of TACP sample is accompanied by decomposition acoustic evidence without damaging the microtest tube.

As described in the previous chapter, the ammonium perchlorate amount is increased over time. Its presence is evident at the DTA thermogram by the endotherm at 241°C, which corresponds to polymorph modification change of ammonium perchlorate (Fig. 7). Also, the maximum of decomposition of TACP stored for 50 days in open air shifts to a higher value over 280°C compared to less than 270°C for freshly prepared TACP.

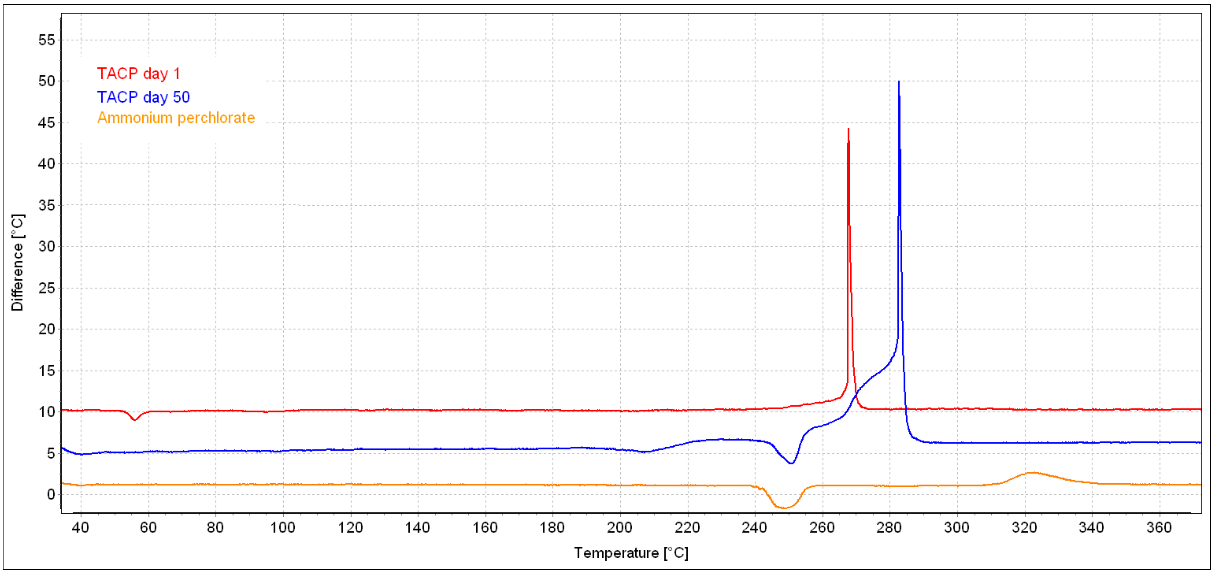

Fig. 7: Comparison of newly prepared TACP and TACP stored for 50 days at open air.

DTA data support the previously described changes monitored by molecular spectroscopy and powder diffraction.

For a deeper understanding of the chemical processes occurring during the heating of TACP, the samples were studied by a combination of thermal analysis methods (TGA-DSC) and mass spectrometry (MS), which was used for the continuous detection and analysis of evolving gases during the thermal decomposition of the sample. Unlike ammonium perchlorate, which completely exothermically decomposes in one TGA step, the decomposition of TACP, as revealed by the thermal analysis results (Fig. 8), is more complex and can be divided into six distinct ranges.

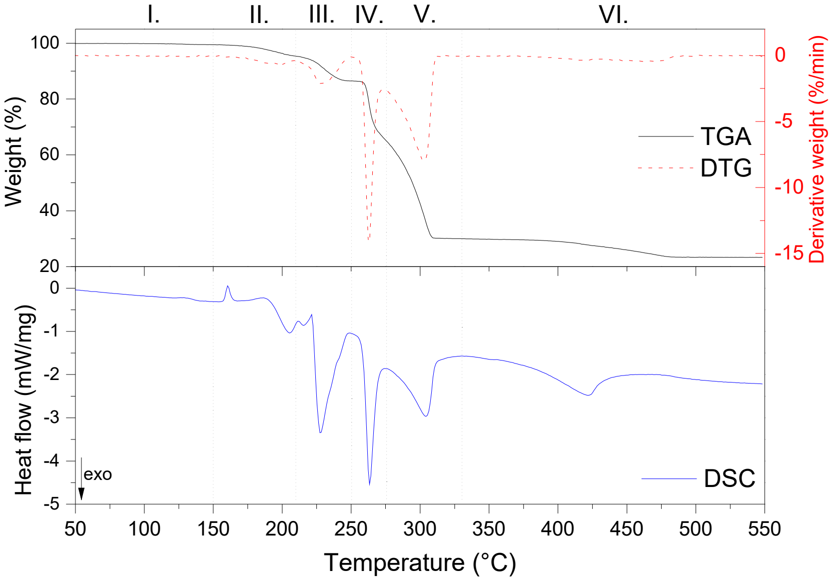

Fig. 8: TGA, DTG, and DSC curves of thermal decomposition of TACP. Temperature range limits are indicated with vertical lines. The values of characteristic temperatures and weight changes in different temperature ranges are summarized in Table 3.

The initial temperature range (range I) is characterized by sample stability. At a temperature of 160°C, a minor endothermic peak, probably corresponding to a phase transformation, is observed. Simultaneous MS analysis (Fig. 9) indicates a release of a negligible quantity of nitrous oxide gas during this process. As the temperature rises, substantial decompositions lead to significant weight loss and pronounced exothermic peaks on the DSC curve. The values of mass changes and temperatures of DTG and DSC peaks are summarized in Table 3.

Table 3: Results of thermal analysis of TACP sample measured under nitrogen atmosphere.

Range	Temperature (°C)	TGA Weight change (%)	DTG Peak temperature (°C)	DSC Peak temperature (°C)
I.	RT – 150	-0.6	-	-
II.	150 – 210	-4.1	200.0	160.4 endo 205.3 exo
III.	210 – 250	-8.8	227.7	215.0 exo

				227.7 exo
IV.	250 – 275	-21.4	263.0	263.3 exo
V.	275 – 330	-35.1	302.8	304.2 exo
VI.	330 – 550	-6.7	-	422.1 exo

MS analysis suggests an initial release of water and ammonia, followed by the detection of oxygen and nitric oxide after surpassing 210°C. Temperatures exceeding 250°C trigger the release of hydrogen chloride. At approximately 315°C, a relatively stable product forms, composed of 40.3% Cu, 49.7% O, and 10% Cl (confirmed by EDX analysis). With further heating (beyond 400°C), exothermic decomposition prevails, culminating in the formation of the final product, CuO (also confirmed by EDX analysis). The final sample weight at 550°C was 23.3%, corresponding to the theoretical CuO content in the TACP sample.

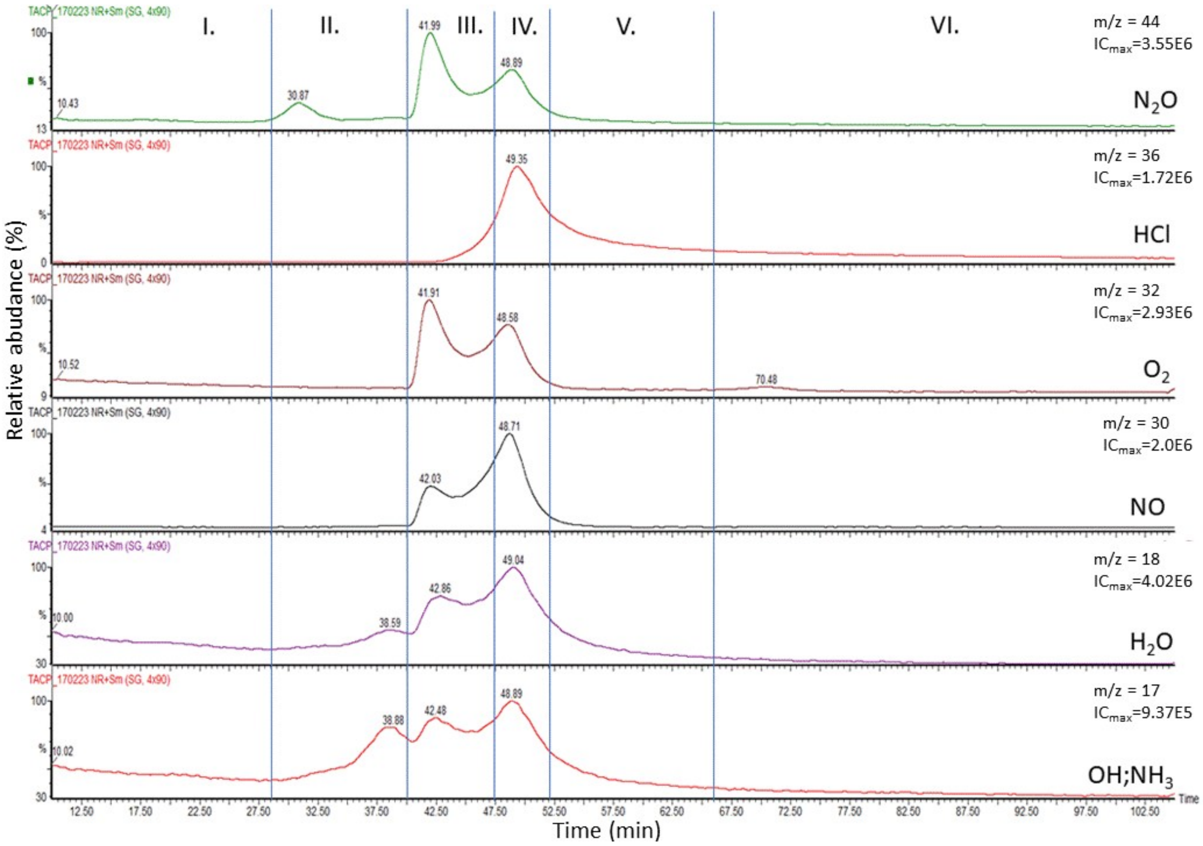

Fig. 9: MS analysis of evaluated gas detected during thermal decomposition of TACP under nitrogen atmosphere. Temperature range limits from TGA/DSC analysis are indicated with vertical lines.

3.2 Analysis of improvised TACP

The simplest method of preparing TACP is by the reaction of cupric perchlorate with an aqueous solution of ammonia. However, as mentioned in the introduction, cupric perchlorate is a relatively poorly available compound, available only from some chemical dealers. Therefore, some TACP producers resort to the improvised *in situ* preparation of cupric perchlorate by reacting copper compounds with ammonium perchlorate or barium perchlorate. Surprisingly, the availability of these two perchlorates is not restricted by EU regulations. Moreover, in the case of poorly available ammonium perchlorate, several improvised procedures for its preparation are published on the Internet. In the following paragraphs, we describe the possible methods suitable for estimating starting materials and thus estimate the way of preparation.

3.2.1 TACP prepared from ammonium perchlorate

The best available copper compounds for improvised preparation of cupric perchlorate according to preparation instructions found on the internet are cupric sulfate pentahydrate (available as a fungicide and herbicide, e.g. used by aquarists for fish treating and against snails), cupric oxide (used as a pigment in ceramics) or malachite (basic cupric carbonate, used as an inorganic pigment).

Cupric sulfate pentahydrate as a copper source

The reaction of cupric sulfate with an aqueous solution of ammonium perchlorate with the subsequent addition of aqueous ammonia solution provides a solid dark blue product with the same shade as pure TACP for all tested molar ratios of $CuSO_4$ / NH_4ClO_4. Based on infrared spectra, the solid product was found to contain mainly TACP and unreacted ammonium perchlorate. The content of TACP$\cdot$1.5H_2O in the reaction product was determined based on the copper content in all samples by atomic absorption spectroscopy. The content of ammonium perchlorate was determined by calculating up to one hundred percent, as the FTIR, Raman and XRPD methods used did not detect the presence of other substances. The results are presented in Table 4.

Table 4: The content of TACP calculated from copper content in the final product of reaction cupric sulfate pentahydrate with ammonium perchlorate with the subsequent addition of aqueous ammonia.

Molar ratio $CuSO_4$ / NH_4ClO_4	Content of copper (wt. %)	Content of TACP$\cdot$1.5H_2O in the sample (wt. %)	Content of NH_4ClO_4 in the sample** (wt. %)
1 : 2*	13.7	77.2	22.8
1 : 4	13.5	75.9	24.1
1 : 10	13.9	78.4	21.6
1 : 20	8.35	47.0	53.0

* Stochiometric ratio

** Content of ammonium perchlorate and potential trace amounts of other impurities not detectable by FTIR, Raman and XRPD

To confirm the use of copper sulfate as a precursor for the improvised preparation of TACP, it is necessary to focus on the presence of sulfate in the prepared TACP. The sulfates can be present either as cupric sulfate or its amine complexes. Using infrared and Raman spectroscopy, sulfates were not visible due to the overlap of the corresponding bands with the TACP bands. Therefore, the presence of sulfates in the product was confirmed using an inductively coupled plasma optical emission spectroscopy (ICP-OES) method. The results are presented in Table 5.

Table 5: The content of sulfates calculated from sulfur content determined using an inductively coupled plasma optical emission spectroscopy in the final product of reaction cupric sulfate pentahydrate with ammonium perchlorate and aqueous ammonia.

Molar ratio $CuSO_4$ / NH_4ClO_4	1 : 2*	1 : 4	1 : 10	1 : 20	TACP standard**
Content of sulfates (wt. %)	0.245	0.156	0.125	0.0616	< 0.000866

* Stochiometric ratio.

** TACP standard prepared by the reaction of cupric perchlorate with ammonia, without the use of cupric sulfate. The result is below the detection limit of the method used.

Even at high excesses of ammonium perchlorate in the reaction mixture, when the sulfate content decreases, the amount of sulfates is several times greater than for TACP prepared by the standard procedure.

Cupric oxide or malachite as a copper source

Other available copper precursors are the insoluble compounds copper oxide and malachite. These compounds dissolve slowly in an aqueous solution of ammonium perchlorate, producing the solution of cupric perchlorate. The dissolution time varied from 3 hours to 72 hours at the stoichiometric ratio of cupric oxide or malachite and ammonium perchlorate. After the subsequent addition of an aqueous ammonia solution to the reaction mixture, the solid product precipitated. In the case of the product from cupric oxide, the resulting product was colored darker than pure TACP, while TACP prepared using malachite visually looks the same as TACP.

Under an optical microscope, the dark crystals containing black copper oxide are indistinctly visible in TACP from cupric oxide, while the green-colored malachite spherical particles are clearly visible in TACP from malachite (Fig. 10).

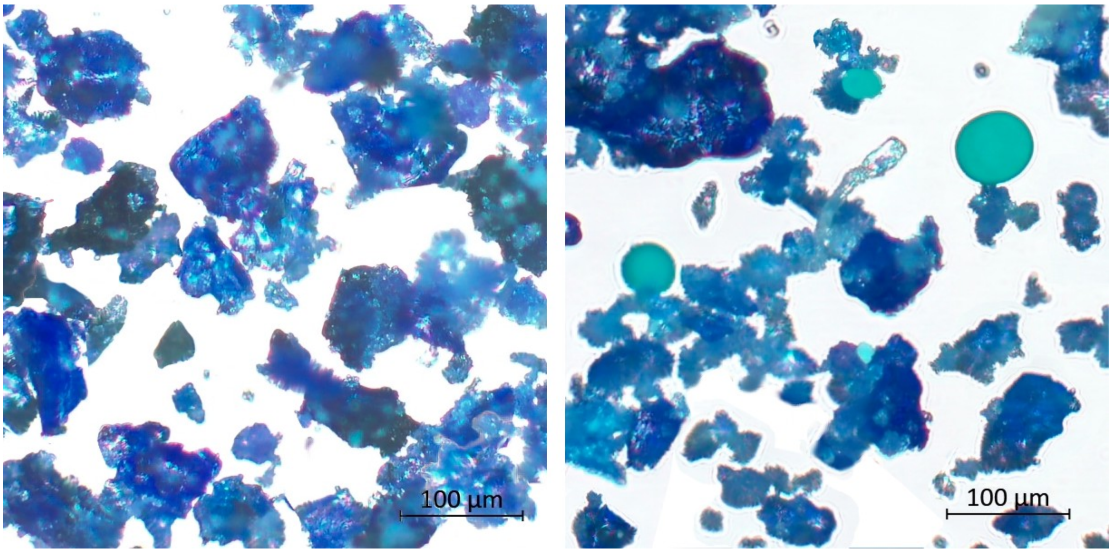

Fig. 10: TACP sample prepared using cupric oxide (left) and malachite (right), the reaction time was 3 hours for both samples.

The SEM images presented in Fig. 11 and Fig. 12 provide confirmation of the presence of cupric oxide and malachite, respectively, in the TACP prepared from cupric oxide and malachite. The distinct lighter coloration of particles, attributed to cupric oxide and malachite, facilitates their clear observation. Notably, malachite particles exhibit a spherical morphology and are noticeably more isolated from TACP particles compared to cupric oxide. For the purpose of EDX analysis (Fig. 11 and 12), designated areas are demarcated on SEM images: area A for cupric oxide or malachite particles, respectively, and area B for TACP particles. Scrutiny of the EDX spectra manifests significant compositional differences in these areas, particularly in the relative intensities of oxygen (O), chlorine (Cl), and copper (Cu) peaks. Corresponding EDX analyses further corroborate the chemical compositions of cupric oxide, malachite, and TACP particles, respectively.

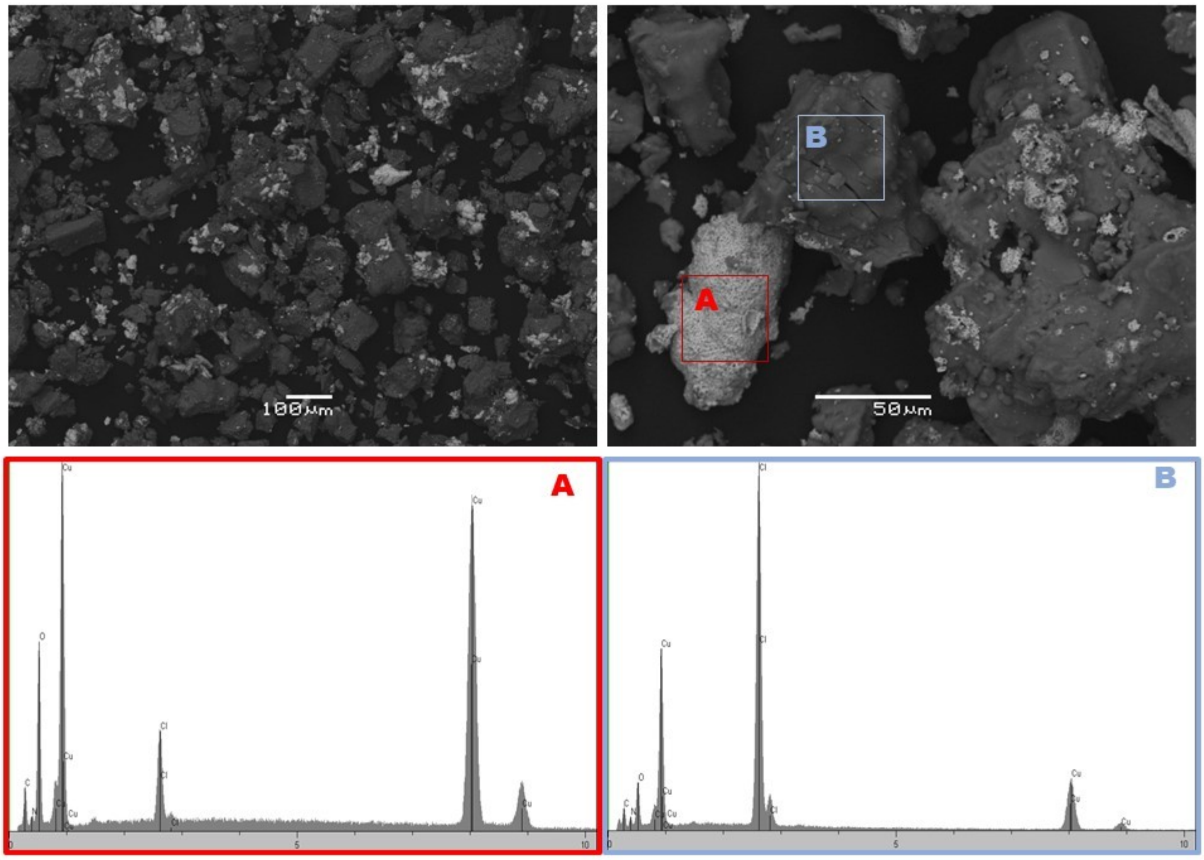

Fig. 11: The SEM images with EDX analysis of the TACP sample containing residual cupric oxide. EDX area and its corresponding spectra of cupric oxide particle (A) and TACP particle (B).

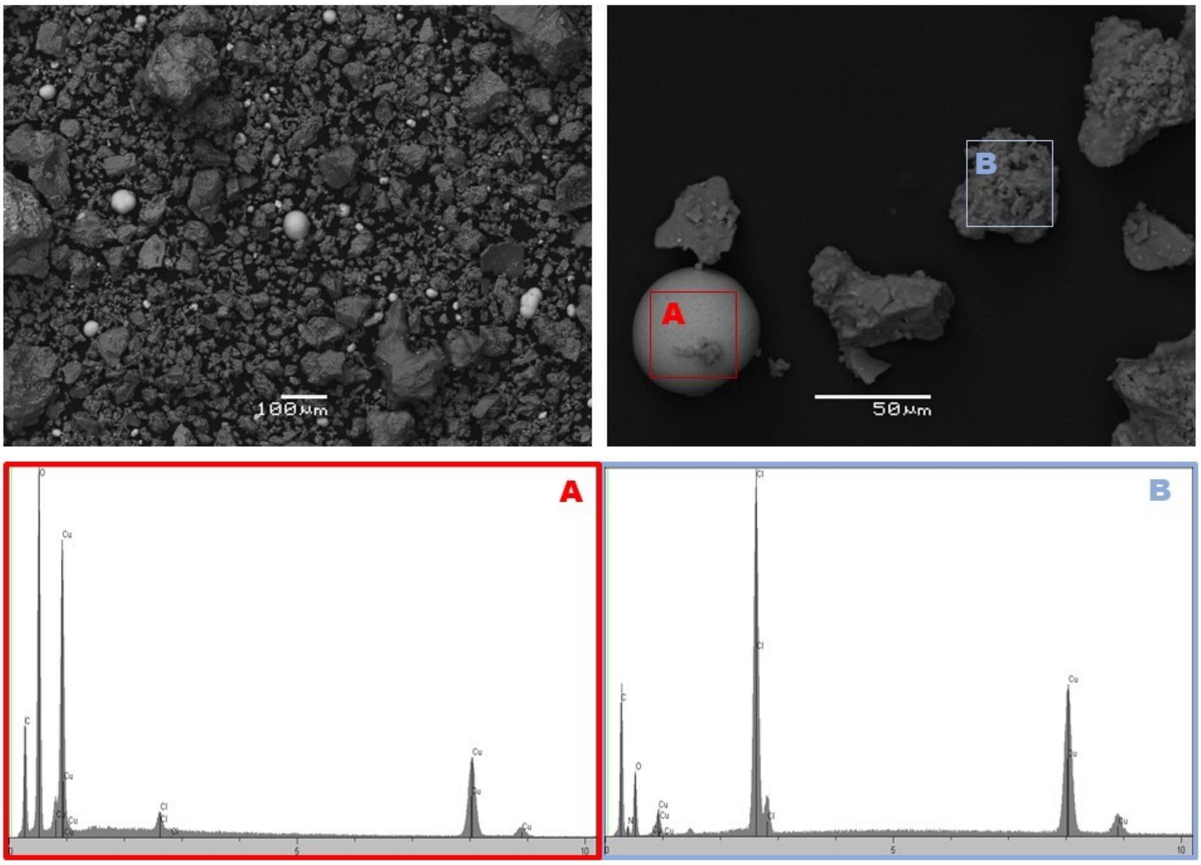

Fig. 12: The SEM images with EDX analysis of the TACP sample containing residual malachite. EDX area and its corresponding spectra of the malachite particle (A) and TACP particle (B).

The unreacted cupric oxide may also be identified in TACP samples by FTIR due to the presence of inverted peaks at 172 cm^{-1} and 151 cm^{-1}. Cupric oxide is detectable in samples with a reaction time of up to 16 hours but hardly visible in samples with a reaction time of 24 hours. The residual cupric oxide was also identified by XRPD in TACP samples prepared with reaction times of 3, 8, and 24 hours. The two strongest peaks at $2\theta=35.52°$(I_{rel} (100%), d=2.525 Å), resp. $2\theta=38.70°$(I_{rel} (70%), d=2.325 Å) were detected and demonstrate the presence of cupric oxide (tenorite - monoclinic form). The amount of cupric oxide in TACP decreases with reaction time. In the case of the TACP prepared from malachite, the presence of malachite in the TACP was not clearly provable by FTIR and XRPD, even for the sample with the shorter reaction time of 3 hours (sample that contains 4.1% malachite).

The quantitative cupric oxide and malachite contents in all samples were determined by the gravimetric method after the removal of soluble TACP by washing it out from the sample. The resulting insoluble cupric oxide and malachite contents in the TACP samples based on reaction time are demonstrated in Fig. 13. In both cases, the content of residual cupric oxide and malachite in TACP decreases with reaction time. Malachite is significantly more reactive to ammonium perchlorate than cuprous oxide, the residual malachite content in TACP decreases to tenths of a percent level after 8 hours of reaction. The unreacted malachite remains at about 0.15% after 16 hours of reaction, and it does not appear to decrease further with increasing reaction time, as the amounts of malachite found for reaction times of 16, 24, and 72 hours are similar within the margin of error.

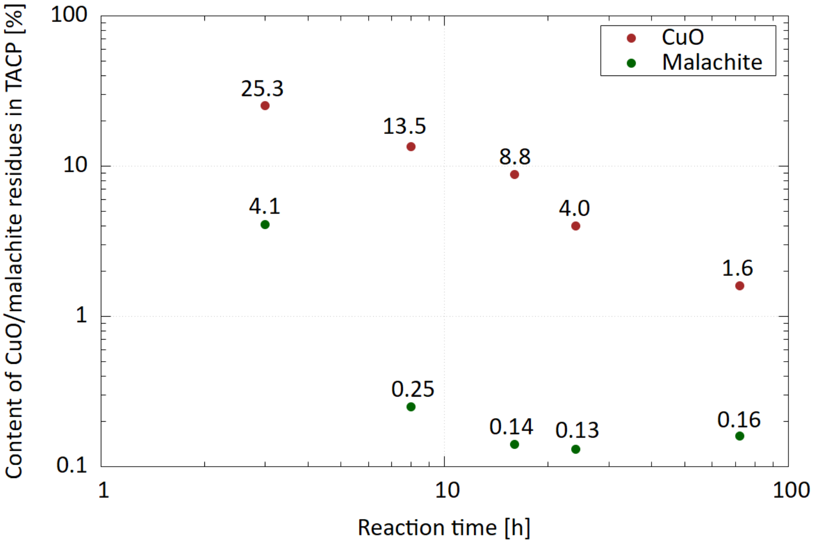

Fig. 13: The content of residual cupric oxide and malachite in solid TACP for samples prepared by the reaction of a stochiometric amount of ammonium perchlorate and cupric oxide or malachite (reaction time on the y-axis) followed by the addition of aqueous ammonia.

3.2.2 TACP prepared from barium perchlorate

A relatively elegant, simple, and on the internet recommended method for the improvised preparation of TACP is the reaction of an aqueous solution of barium perchlorate with an aqueous solution of cupric sulfate. Barium sulfate precipitates, and formed cupric perchlorate remains in the solution. After filtration or decantation of barium sulfate precipitate, TACP easily crystallizes after the addition of aqueous ammonia.

The clues indicating the use of this method is the higher barium content in TACP. The results of the determination of the trace barium content in the final TACP prepared using a variety of stoichiometries are given in Table 6.

Table 6: The content of barium in TACP prepared by the reaction cupric sulfate pentahydrate with barium perchlorate with subsequent reaction of the filtrate with aqueous ammonia.

Excess/lack of $Ba(ClO_4)$ against $CuSO_4$ (wt. %)	Content of barium in TACP (mg/kg)
+ 20	10,780
+ 10	1,760
0	729
- 10	1,260
- 20	1,070
the common procedure*	67.7

* TACP prepared by a common procedure as described in the experimental part by the reaction of cupric perchlorate with aqueous ammonia (without barium perchlorate)

A high content of barium (729 – 10,780 mg/kg) was found in all TACP samples prepared using barium perchlorate. This barium content is one to two orders of magnitude higher than for the TACP sample prepared by the common method without barium perchlorate (67.7 mg/kg). As expected, the barium content in TACP increases with the excess of barium perchlorate over stoichiometry. In contrast, it is interesting to note that a high barium content was also found in samples where barium perchlorate was used in deficiency compared to stoichiometry, i.e. under conditions where all barium in the form of barium sulfate should have been completely precipitated.

3.3 Detection of TACP by dogs

The results of target odor testing using a dog are summarized in Table 7. In the case of TACP, a high level of detection confidence was achieved in 47 positive trials out of 50. Based on these results, the dog is able to remember and discriminate the TACP odor. Owing to the low chemical stability of TACP, we expected that what the dog perceives in the TACP odor is predominantly ammonia that is gradually released from TACP during aging.

Table 7: The results of target odor testing using a dog.

Target compound	Positive detection	Negative detection	Sensitivity	Specificity	Accuracy
TACP	47	3	0.94	0.992	0.985
TACN	0	25	0	0.875	0.778
$(NH_4)_2CO_3$	7	18	0.28	0.907	0.835
NH_4ClO_4	1	24	0.04	0.879	0.786
NH_4Cl	0	25	0	0.875	0.778
$(NH_4)_2SO_4$	0	25	0	0.875	0.778

Positive detection = the dog correctly marked the target odor; Negative detection = the dog did not mark the target odor; Sensitivity = the ability of a dog to correctly identify the target odor; Specificity = the ability of a dog to correctly determine the non-target odors (and not mark them); Accuracy = the ability to differentiate the target and non-target odors correctly.

We did not include pure ammonia in the tests because of its toxicity. Instead, we used ammonium salts, which also release ammonia but do not reach dangerous concentrations above the sample. We, therefore, included ammonium sulfate, chloride, and carbonate as additional target substances. Of these substances, the dog reacted positively in 28% of trials with ammonium carbonate, whereas it did not react at all to ammonium chloride and sulfate. The reason for some mistakes in ammonium carbonate is that it slowly decomposes to ammonia, carbon dioxide, and water, producing the characteristic ammonia odor. In contrast, ammonium chloride and ammonium sulfate, which the dog does not react to, only release ammonia when heated to higher temperatures. After the dog's positive reaction to ammonium carbonate, the dog was not rewarded during the testing. As a result, the dog reacted negatively to ammonium carbonate in the subsequent trial. In the following trial, the intensity of the ammonia odor from the carbonate was significantly reduced by removing the sniffer with ammonium carbonate from the can, leaving only a residual ammonia odor in the can. In two cases, the dog responded positively to the can, supporting the assumption that the dog primarily perceives the ammonia odor in the TACP.

TACN was tested as a target odor because of its structural similarity to TACP, which, like TACP, could release ammonia and thus be of interest to the dog. In this case, the assumption was not confirmed, and the dog did not react to TACN.

The last of the target substances was ammonium perchlorate. This compound was tested for its formation in the decomposing TACP. The dog reacted negatively to ammonium perchlorate in twenty-four cases out of twenty-five trials (96%). The most likely reasons for this could be either the low ammonium perchlorate content in the TACP (the sample was closed during storage, slowing its degradation) or the masking of the ammonium perchlorate odor by ammonia.

This preliminary study aimed to test the ability of dogs to detect the scent signature of TACP. However, since imprinting an inappropriate chemical odorant could compromise the working abilities of a service dog, the test was conducted with only one dog. A study involving a larger number of dogs would be required to refine, confirm, or refute the results.

3.4 Analysis of TACP post-blast residues

SEM has been chosen as the elemental analysis method for post-blast residues (PBR) analysis, as it is usually available in most forensic laboratories due to its use in gunshot residues analysis. Post-blast residues collected after the detonation of TACP (Fig. 14) are of an ordinary shape and do not exhibit any specific morphology. It has been found that copper and chlorine atoms are present together in relatively high amounts compared to background elements. From a forensic point of view, this presence of copper and chlorine in samples collected from the blast scene can be considered a marker of TACP usage. No commonly used homemade explosive known to us, other than TACP, contains the combination of those two elements so clearly presented in post-blast residue particles. It should be noted that the only conceivable explosive with a combination of chlorine and copper is a cupric salt of 5-chlorotetrazole. However, this industrially manufactured primary explosive used in the past [61] is a difficult-to-prepare substance and, to our knowledge, is not being used as a homemade explosive.

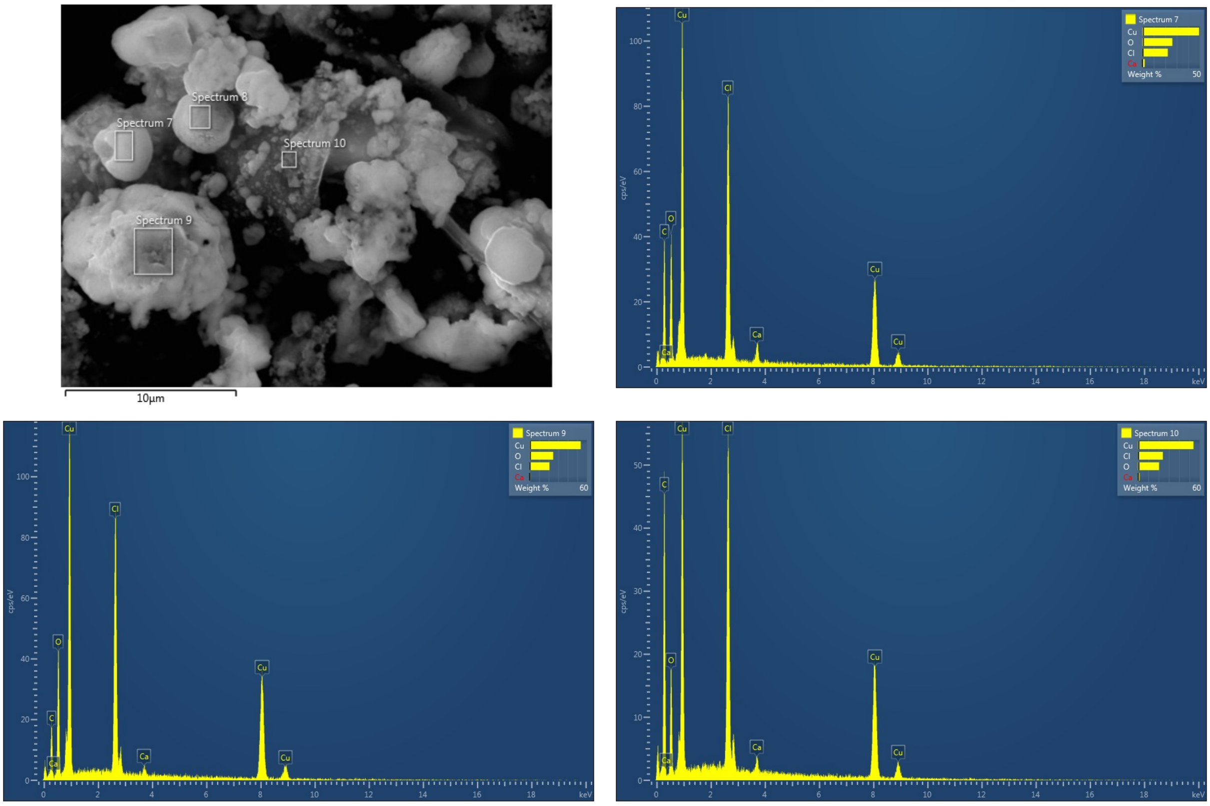

Fig. 14: SEM analysis of post-blast residues obtained after TACP detonation.

Other methods for post-blast residue analysis, such as ion analysis, could also be considered. Ion chromatography is a widely recommended method for PBR ion analysis; however, as this method was not available to us at the time of working on this study, we are unable to provide further details on its usage in this case. PBR field test strips (for example MQuant® Chloride Test and Quantofix® for semiquantitative determination of cooper) can also be used as further confirmation (Fig. 15). The mere presence of perchlorate or ammonium ions cannot be considered evidence for the use of TACP. Traces of these ions observed in post-blast residues may originate from other compounds, such as ammonium perchlorate, used as an oxidizer. However, the demonstration of these ions, particularly in combination with elemental analysis confirming the presence of chlorine and copper, can be considered strong indicators of the possible use of TACP.

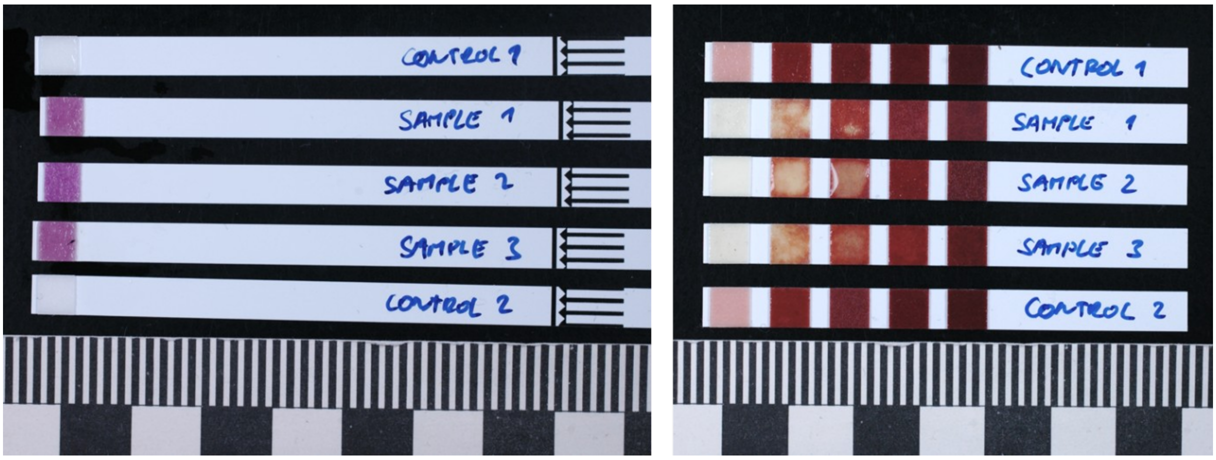

Fig. 15: Positive results of a field test strips indicate the presence of chloride (sample 1-3, left) and copper (sample 1-3, right) in TACP post-blast residues.

4 Conclusions

The typical forensic analytical methods such as infrared and Raman spectroscopy, powder X-ray diffraction supported by elemental analysis, and thermal analytical methods may be used for the identification of TACP. It is important to consider that TACP can vary in its composition due to different content of hydrate water or the presence of ammonium perchlorate in stored products. TACP is a chemically unstable compound that decomposes in open air to ammonia, ammonium perchlorate, and basic cupric perchlorate in a matter of months.

Identifying impurities in homemade TACP can help to identify the precursors and preparation method used for its production. Four improvised methods of preparing TACP can be successfully recognized. If copper sulfate is used as a precursor, the presence of sulfates can be detected in TACP. Similarly, the presence of barium in TACP indicates the use of barium perchlorate as a precursor. The optical or electron microscopy with EDX analysis can be used to identify solid residues of insoluble copper compounds such as copper oxide or malachite. Higher contents of these precursors can be detected by XRPD and FTIR.

The results of canine detection of TACP suggest that the dog is capable of detecting TACP. The dog is likely targeting the ammonia odor in TACP, which may lead to the positive detection of ammonia or ammonia-releasing substances.

The presence of high levels of copper and chlorine atoms in post-blast residues can help identify TACP in case of post-blast detection. This combination of only these two heavier atoms in the post-blast residues is highly unlikely to be found in other commonly used homemade explosives.

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