IWEM 2018
International Workshop on Energetic Materials
18-19 October 2018

Abstract Book

Istanbul/TURKEY

International Workshop on Energetic Materials
18-19 October, 2018, Istanbul, Turkey

Dear IWEM2018 attendees,

"International Workshop on Energetic Materials-IWEM 2018" was held between 18-19 October 2018 under the co-chairmanship of Prof. Dr. Reşat APAK and Assoc. Prof. Dr. Ayşem ARDA in the Blue Hall of the Rectorate Building of Istanbul University within the scope of the IUPAC project "2015-008-2-500". The opening ceremony of the Workshop was held by Rector Prof. Dr. Nuri AYDIN and Vice Rector of Istanbul University-Cerrahpaşa Prof. Dr. Mehmet BİLGİN. As IUPAC project partners, Prof. Dr. Jean Claude-TABET (Sorbonne University-France), Prof. Dr. Wujian MIAO (University of Southern Mississippi-USA), Assoc. Prof. Dr. Manel Del VALLE (Autonomous University of Barcelona-SPAIN), Assoc. Prof. Dr. Prof. Dr. Jose Gonzalez-RODRIGUEZ- (University of Lincoln, UK) and also Prof. Dr. İbrahim DİNÇER from University of Ontario-Canada, and Head of TUBITAK-SAVTAG (Turkish Scientific Technological Research Council-Defense Technological Research & Development Division) Colonel Dr. Mustafa CİVELEK participated. Additionally, experts from the Presidency of Turkish General Staff, TUBITAK-SAGE, TUBITAK-MAM, ROKETSAN AS, ALTINAY Aviation and Advanced Technologies Inc., Istanbul University-Cerrahpasa, Baskent University, Kirikkale University, Ondokuz Mayis University, Hacettepe University and Gazi University related to the field actively took part in the Workshop with (mostly) oral and poster presentations.

IWEM2018 started with the opening speeches of the Rector of Istanbul University-Cerrahpaşa, Prof Dr. Nuri Aydın, and the Co-Chairman of IWEM2018 Prof. Dr. Reşat APAK. Then, Assoc. Prof. Dr. Sevil ULUCAN WEINSTEIN and her team from Istanbul University-State Conservatory performed a violin concert.

During IWEM2018, the following presentations were made: Studies on the detection energetic materials in the environment were reported by Prof. Dr. Reşat APAK, Assoc. Prof. Dr. Ayşem ARDA and research team (orally presented by Prof. APAK) under the title of "Examples of Colorimetric and Electrochemical Sensors/Nanoprobes (Devised in Istanbul Univ.) for Determination of Energetic Materials; "Overview of Novel Hydrogen and Ammonia Production Research at CERL" by Prof. Dr. İbrahim DİNÇER as Plenary Lecturer; "Mass spectrometry detection of nitro explosives" by Prof. Dr. Jean Claude-TABET, (Sorbonne University-France; IUPAC Project Partner) as a Keynote Lecturer; "Trace detection of explosives based on electrochemical, chemiluminescent, and electrogenerated chemiluminescent techniques" by Prof. Dr. Wujian MIAO (University of Southern Mississippi-USA, IUPAC Project Partner) as a Keynote Lecturer; "Development of molecularly imprinted polymers for the sensor-based detection of explosives" by Assoc. Prof. Dr. Manel Del VALLE (Autonomous University of Barcelona-SPAIN, IUPAC Project Partner) as a Keynote Lecturer, "Identification and detection of home-made and most common improvised explosives used in terrorist attacks by chromatographic and spectroscopic techniques" by Assoc. Prof. Dr. Jose Gonzalez-RODRIGUEZ- (University of Lincoln-UK, IUPAC Project Partner) as a Keynote Lecturer.

A total number of 55 researchers have attended the IWEM2018; the Workshop was successfully completed with the oral presentations of 15 invited speakers from different universities and organizations, totaling 20 oral and 9 poster presentations with positive feedbacks from the attendees at the end (closing panel). The Workshop hosted scientific discussions having the potential for further cooperation possibilities among heterogenous research groups.

Prof. Dr. Reşat APAK and Assoc. Prof. Ayşem ARDA

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Plenary Lecturer

PL

Overview of Novel Hydrogen and Ammonia Production Research at CERL

İbrahim Dinçer

University of Ontario, Canada

For the past ten years we have been performing cutting-edge research on the development, modeling, analysis, building and testing of novel hydrogen and ammonia production systems at the Clean Energy Research Laboratory (CERL) in the Faculty of Engineering and Applied Science of University of Ontario Institute of Technology (UOIT). These systems are essentially critical for non-fossil fuels based and hence sustainable solutions for the targeted hydrogen economy and offer carbon-free technologies for the province of Ontario in specific and the world at large. For hydrogen production, the research primarily focuses on thermochemical and hybrid cycles, photoelectrolysis, pohotocatalysis, and photoelectrochemical processes and related technologies. In regards to ammonia production, the focus is essentially put on electrolysis, gasification and electrochemical based systems. Such systems and related technologies are developed to be brought to the commercialization phases for the local and international markets. This particular presentation will discuss all these clean hydrogen and ammonia production systems and related technologies as well as their applications in various sectors, ranging from transportation to industrial.

Keynote Lecturer

KL-1

Examples of Colorimetric and Electrochemical Sensors/Nanoprobes (Devised in Istanbul Univ.) for Determination of Energetic Materials

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In view of the vapor pressures of the nitro-explosives 10^{-6}-10^{-9} torr there are no commercialized detectors for their vapor phase detection. In this case, it is important to develop sensitive optical sensors and nanoprobes for the detection of these energetic substances. Some examples of the energetic material sensors which were developed by our laboratory, Colored Meisenheimer anion formed from TNT in basic media actually an unstable structure thus its made stable in IBMK organic phase[1]. Also, solid phase extraction (SPE) of the Meisenheimer anion of TNT formed in alkaline solution onto a strongly basic anion exchange resin Dowex 1 X8 (OH^--form) enabled the stabilization of the orange-red color formed both in the solid resin and aqueous solution phases, suitable for colorimetric measurement[2]. The charge-transfer reagent, dicyclohexylamine, was entrapped in a polyvinylchloride polymer matrix plasticised with dioctylphtalate, and moulded into a transparent sensor membrane sliced into test strips capable of specifically sensing TNT. Acid hydrolysis of peroxide-based explosives yields hydrogen peroxide, which can be colorimetrically measured with a Cu(II)-neocuproine-impregnated Nafion (perfluorosulfonate polymer) sensor[4]. In the an another work, acid hydrolysis of TATP yields H_2O_2; pH adjusted to 3.6, and magnetite nanoparticles (Fe_3O_4 MNPs) added to the medium to produce •OH from H_2O_2, due to peroxidase-like activity of MNPs. Finally pink-colored DMPD-quinone cation radicals are retained on Nafion[5]. Zero-valent silver nanoparticles (Ag^0NPs) can be partly oxidized by H_2O_2 to Ag^+ which can in turn oxidize TMB (3,3′,5,5′-tetramethylbenzidine) to the blue-colored diimine absorbing at 655 nm. The hydrolytic degradation of TATP to hydrogen peroxide using a strongly acidic cation exchanger resin Amberlyst-15 may be preferred for field use[6]. Identities of unknown explosives found in the field could be determined with specially designed colorimetric kits by observing their colour change after spraying appropriate reagents onto a chromatographic paper containing explosive residues following vaporization of acetone used as solvent for SPE[7]. Nitramine-type explosives RDX and HMX were determined colorimetrically with the aid of a gold nanoparticle (AuNP) sensor modified with 4-aminothiophenol after kinetic hydrolysis[8]. Electrochemical sensor was designed for detecting nitroaromatic- and nitramine-type energetic materials, relying on gold nanoparticles (Au_{nano}), modified glassy carbon (GC) electrode coated with nitro-energetic memory-poly(carbazole-aniline) copolymer (Cz- co-ANI) film (e.g., TNT memory-GC/P(Cz- co-ANI)-Au_{nano} modified electrode)[9]. The working principle of the latest TNT/tetryl sensor is charge-transfer (CT) interaction between the electron-rich free amino ($–NH_2$) group of DACH and the electron-deficient $–NO_2$ groups of TNT/tetryl, added to possible nanoparticle agglomerization via electrostatic interaction of TNT-Meisenheimer anions with more than one cationic DACH-modified AuNPs[10].

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KL-2

Mass Spectrometry Detection of Nitro Explosives

Jean Claude-Tabet

Sorbonne University-France

KL-3

Trace Detection of Explosives Based on Electrochemical, Chemiluminescent, and Electrogenerated Chemiluminescent Techniques

Wujian MIAO

University of Southern Mississippi-USA

KL-4

Development of Molecularly Imprinted Polymers for the Sensor-Based Detection of Explosives

Anna Herrera-Chacon and Manel del Valle

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Analysis of explosive compounds, especially for security purposes, needs achieving the lowest possible detection range, at least at the sub-ppb level. If the maximum simplicity, minimum cost and widest deployment are sought, detection using chemosensors or biosensors is the proper choice. Biosensing using particular recognition elements achieves the sensitivity requirements needed, but do not solve completely the problem. The use of antibodies prevents reutilization of used devices, because recognition is normally irreversible. The use of aptamers, also with good performance, implies following different wet stages, then don't satisfy the one-step, more simple approach.

Analytical techniques permitting a straightforward and direct sensing protocol, on the other hand are limited in their detection ability. The use of a highly selective enrichment material can be one way to accomplish the sensitivity requirements, and here arises the idea of Molecularly Imprinted Polymers (MIPs), as these can be used employing separation principles to improve performance and allow detection of explosive compounds with security concerns. As the most interesting property of MIPs it is to be stressed that they can be tailor-made to interact with a given chemical with great flexibility. All this make MIPs an option of choice, especially in HPLC as a selective column material, or in sample pretreatment, adopting a solid phase extraction approach.

But also, a MIP can be a recognition element in a (bio)sensor, accomplishing in this way the above commented requirements. The sensing variants that can be made compatible with MIPs are mainly optical: e.g. absorbance or fluorescence when displacement of a previously loaded labelled analogue is used. In the case of common explosive compounds, being these highly oxidizing agents, electrochemistry can be also used, achieving in this way a high simplicity of operation. Voltammetric sensors with simple electrodes, or more elaborated ones if special modifiers are used can be a pocket, simple, transportable and of easy handling detector, only it is difficult to detect concentrations below the ppm. Integration of a custom made MIP into a voltammetric sensor can be one of the solutions, if some previous enrichment stage is adopted, as interferents will then be rejected, and detection limits reduced to the demanded levels. Recent work in our laboratory developed a MIP-based biosensor for trinitrotoluene (TNT), integrating the recognition element with a voltammetric sensor. To obtain the MIP, the more easily available analogue dinitrophenol (DNP) was the template used. Characterization results of the developed sensor towards DNP and TNT will be shown, with improvements of sensitivity of TNT of ca. a factor of 10, when a 10 min enrichment time was used.

KL-5

Identification and Detection of Home-Made and Most Common Improvised Explosives Used in Terrorist Attacks by Chromatographic and Spectroscopic Techniques

Jose Gonzalez-RODRIGUEZ

University of Lincoln-UK

A recent document produced by Action on Armed Violence (AOAV) on the number of deaths caused by explosions in 2017 reported an alarming number of casualties suffered as a consequence of the action of explosives with 56% of all casualties caused by Improvised Explosive Devices (IEDs).

When preparing IEDS two scenarios are possible: an explosive that is easy to manufacture and detonate using home-made detonators or low intensity explosives but its stability make it difficult to safely handle it (i.e. TATP, HMTD, MEKP). The presence of multiple peroxide groups in the structure of these molecules make them highly unstable and detonation or deflagration (depending on the confinement and amount of the explosive) can easily occur by friction, percussion, electrical or thermal activation. A second option, such as In the case of Ammonium Nitrate Fuel Oil (ANFO), where the explosives are also easy to manufacture and more stable but their detonation requires the use of a more sophisticated detonator. ANFO is usually formulated as 95% NH_4NO_3 and 5% Fuel Oil. ANFO is classified as a tertiary high explosive according to its sensitivity and velocity. The mixed product is considerably safe, insensitive, easy to handle and easy to deliver in mining or industrial environments. At present, approximately 70% of explosive market is taken by ANFO.

Being one of the most common analytical techniques found in forensic laboratories around the world, chromatographic methods are still at the forefront for the detection of explosives and still considered the most important confirmation technique when Court procedures are involved. Hyphenation with different detectors makes this technique a powerful tool for benchtop detection. An important shortcoming appears when the technique needs to be used in the field or for fast analyses and portable systems are required. Recent advances in miniaturisation of instruments are making this less of a problem but more research and commercial systems are still needed.

Spectroscopic techniques have been widely sought for the detection of home-made explosive devices due to their inherent characteristics which made methods based on them fast, portable, selective, relatively cheap (when compared to other techniques) and most important, direct non-destructive analysis (desirable from a forensic point of view). The ability to offer an answer without the need to proceed to preparation or separation of the sample makes them a very suitable alternative to chromatographic methods. The drawback lies on their exposure to matrix effect, lack of sensitivity or presence of masking interferences. Some of these have been solved by the use of chemometric and multivariate analysis to perform mathematical post-sample data treatment in order to enhance the signal or fingerprinting. Some of these techniques are now being adapted for stand-off detection, which open the door for military use or civilian protection. Although there is considerable research in this field and laboratory tests are highly successful, the reality is that stand-off detection is far from being a field technique at present. This may be due to the variability of conditions which may affect the signal and low performance rate in the field. A greater use of signal filtering and chemometric treatment might have a big impact in getting this technique to real operational levels.

Invited Lecturer

IL-1

Future Characterics of Energetics Materials (EM)

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Main Safety For Cars

How do you open/works the airbag?
1. When the car is subjected to impact, suddenly speed is losing.
2. Electronic sensors detect speed change.
3. The accelerometer measures the degree of impact.
4.The airbag is triggered if the car is subject to severe forces.
5. Explosive is filled with nitrogen or argon gas that is suitable for airbag.
6. After 30-40 milliseconds from the accident, Explosive activeted and the airbag is inflated.
For safety reason!

We believe the explosives for safety reason. And WHY? We don't still consider as its are good items?

The problems of the scientist's for self-confidence in EM
(There is no enough research for new energetic ingredients)
Preventing the problems of explosive's logistics from EM research,
(After 20-30 years of explosive storage without being paid attention the hot, cold, moisture, sunny conditions; it's look the explosion is dangerous?
After 30 years storage, which active product can remain safe?)
Explosives is not iron or copper? It is not the fault of the material that the administrators do not know the Explosives Reality.
More… EM not directly Explosives!!!!

More green energetic ingredients make more safer Explosives and make more green world.

These following problems are not related with the main EM research activities; but all the negatives effect still blocs the research.

Munitions containers and packaging material,
Munitions debris remaining after fire,
Demilitarization residue,
Disposal and range-related debris,
Absence of enough explosives safety documentation,
Life Cycle Demilitarization Considerations

This case study show us clearly that,
All activities for EM must be in professionally and especially with very qualified persons.

IL-2

Alternative Inert Plasticizers for Polymer Bonded Explosives

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Mechanical, thermal and sensitivity properties of Plastic Bonded Explosives (PBX) depend on the type of ingredients in their formulation. Aim of this study is to find alternative inert plasticizers for high performance polyurethane (PU) based cast PBX formulations to have similar or better properties than older formulations without compromising their IM properties. Although very small portion of total production of plasticizers is used for explosive formulations, they play very significant role in that area. Plasticizers have involved explosive formulations to improve process parameters, mechanical properties and even insensitivity properties of them. PBXN-109 is the most widely used plastic bonded explosive because of its high impulse effect. Because of its extensive usage and importance among other PBX formulations, studies are particularly focused on PBXN-109 formulation. Isodecyl pelargonate (IDP) and dioctyl adipate (DOA) are the most preferred inert plasticizers in polyurethane based thermoset explosive formulations. In addition to them diisononyl adipate (DINA) and diisononyl phthalate (DINP) were used and screened as inert plasticizer candidates for aluminized cast PBX formulations. Mechanical, thermal, and sensitivity properties of PBX formulations were studied and compared in detail.

Keywords: Plasticizer, PBX, Explosive, mechanical properties, thermal properties, insensitivity

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IL-3

Hazard Assessment of Combustion Products of Energetic Materials

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During the use of ammunition and other energetic material containing weapons, millitary personnel can be exposed to hazardous chemicals. In order to reduce the risks, understanding the physical phenomena with chemical reactions and quantifying them is necessary.
The composition of combustion products within a gun barrel is calculated by using NASA CEA equilibrium combustion computer code. Change of chemical composition by pressure is introduced and pressure dependency of toxic gases is shown. Application of possible technical solutions is offered in order to reduce toxic hydrogen cyanide concentration based upon its pressure dependency.
Combustion products of two explosive material is calculated by using Explo5 equilibrium combustion computer program.
Experimental measurements found in literature shows that complex compounds are produced in quite small quantities, which cannot be calculated by any of the present equilibrium combustion computer code, where further research for the gap is currently performed at technical group of NATO AVT-277.

Keywords: Energetic Material, Equilibrium Combustion, Hydrogen Cyanide

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IL-4

Production of Metal Matrix Composites by Infiltration Method

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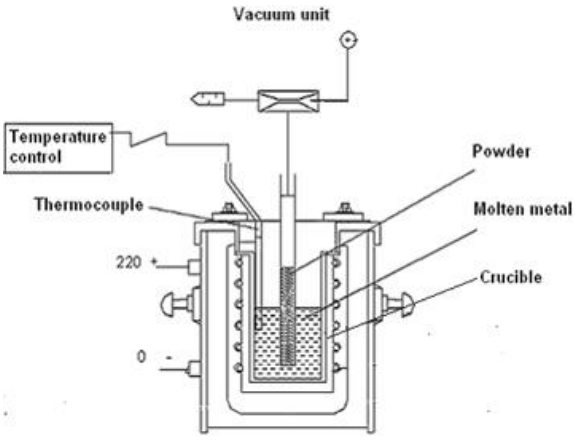
The production of aluminum matrix composites by infiltration method and effect of the properties of the material are emphasized. One of the contents of the aluminum matrix composite is alumium / aluminum alloys, while the other ingredients are non-metallic, usually ceramic reinforcement elements such as B_4C, SiC, MgO, TiB_2, RHA and Al_2O_3. [1-2] Aluminum matrix composites have started to attract attention in many areas such as aerospace, automotive and aerospace thanks to their low weight, high strength, high hardness, high modulus, and very good wear resistance[3]. Moreover, the properties of these composites can be tailored by changing the fraction, size and type of reinforcing particles. The parts produced from AMC have a longer life, less energy and lower emissions. In addition, when used in automotive and aerospace vehicles, all the weight, fuel consumption and pollution have been reduced. Aluminum matrix composites are produced by solid metal processes or by liquid metal processes. Solid metal processes give good results but are expensive. Liquid metal processes can be more economical. However, if the ceramic particles are not well wetted by the molten metal, obstacles such as poor ceramic / metal interfaces and incomplete infiltration may occur. The process of infiltration is generally used as a liquid metal process and is carried out in a pressure or vacuum.[4]



Infiltration process involves holding a porous body of the reinforcing phase within a mold and infiltrating it with molten metal that flows through preform to fill the pores and produce a composite. Liquid metal generally does not spontaneously wet the reinforcement. Therefore, it is often forced into the preform by application of an external force that overcomes the capillary and fluid-drag forces.

Pressureless (free) infiltration, pressure infiltration and vacuum infiltration techniques take part in producing metal matrix composites. Vacuum infiltration process ensures enhanced wetting, and thus the good metal-ceramic interface bonding could be achieved [5].

Keywords: aluminium, composite, reinforcement, infiltration, vacuum

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IL-5

Electrochemical Sensor for Picric Acid Detection

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Graphene, the thinnest two dimensional carbon material, has become the subject of intensive investigation in various research fi elds because of its remarkable electronic, mechanical, optical and thermal properties[1]. Molecularly imprinted polymers are very suitable for fabricating chemical/biological sensors with enhanced selectivity. The advantages of using polymer and graphene composites as sensing material can be expressed with respect to increased surface area, higher numbers of analytical recognition sites, low resistance and improved environmental stability, due to the unique properties of both components.

Graphene and/or reduced graphene oxide are able to be prepared by an electrochemical method which is effective and green route[2]. Graphene oxide reduction and electropolymerization of a monomer in the presence of template molecule are usually performed by separate procedures. Here in this work electropolymerization of aniline and electrochemical reduction of graphene oxide were taken place simultaneously.

It is aimed to detect picric acid using an electrochemical sensor based on graphene and molecular imprinted polymer (MIP). The reduction of the synthesized graphene oxide and polymer formation were carried out electrochemically using cyclic voltammetry by scanning 15 cycles in the potential range of -1.0 to + 1.2V (vs Ag / AgCl) as a one step process. The methanol-acetic acid mixture was used to remove the repressed picric acid from the sensor and the experimental conditions were optimized.

After the sensor was developed, square wave voltammetry, SEM and electrochemical impedance measurements were used for characterization. The prepared new composite film possessed the advantages of both polyaniline and reduced graphene oxide with a synergistic effect, which has excellent electrocatalytic activity.

Keywords: moleculary imprinted polymer, graphene, trinitrotoluene

Acknowledgment: This work is supported by Ondokuz Mayıs University (Project Number PYO.FEN.1904.17.001)

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IL-6

LIBS for Energetic Materials Detection

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Prevention of explosives requires sensitive and selective detection systems. Common techniques for detection of bulk explosives are X-ray analysis, neutron activation or scattering and imaging methods based on nuclear technology. However, detection of trace explosives is more complex issue due to using of wide variety of materials in explosives. Most widely accepted techniques can be listed as ion-mobility spectrometry (IMS) and gas chromatography (GC). Although these methods are quite reliable and sensitive, their principal based on vapor analysis and detection of small concentration in especially good sealing conditions is quite hard. Therefore, it is required urgently more sensitive, stand-off and rapid systems. Laser induced breakdown spectroscopy has become a valuable tool in recent years for explosive detection. It is an atomic emission spectroscopy technique which provides multi-elemental analysis in solid, liquid and gasses. In comparison with conventional elemental analysis methods such as inductively coupled plasma-mass spectroscopy (ICP-MS), atomic absorption spectroscopy (AAS) and X ray fluorescence spectroscopy (XRF), it has much more advantages which can be listed as no/min. sample preparation procedures and rapid, in-situ and real time analysis opportunities. In the literature, black powder, TNT, PETN, HMX, RDX, C4 and other kinds of explosives were studied by LIBS. All of these energetic materials give unique spectrum due to their different elemental composition, elemental ratios and molecular bands. Therefore, C2, H, O, N elements and H/C2, O/H, O/K, O/N, Na/C2 ratios can be indicative in explosives. On the other hand, due to the frequent use of nitrate in the construction of explosives, the agricultural and fertilizer sector has been negatively affected by the prohibition of nitrate fertilizers in Turkey. Therefore, LIBS can be a promising tool for also identification of fertilizers and high nitrate containing fertilizers. In this study, the application potential of LIBS for explosive detection were presented.

Keywords: LIBS, explosives, nitrogen, fertilizer, nitrate

IL-7

Surface-enhanced Raman substrates for rapid detection of explosives

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Surface Enhanced Raman Spectroscopy (SERS) takes the advantages of strongly increased Raman scattering signal generated by local field enhancements near metallic nanostructures. The internal modes of the reporter molecule can be used as diagnosis signals and appropriate placement of the reporter molecule on the metal nanoparticle surface is a well known challenge. Several approaches have been suggested for this purpose and multipurpose functionalized hybrid nanoparticles are very promising for the detection of trace amounts of analyte. Simple and fast generation of nanoparticles and nanostructured films with appropriate probe provide SERS applications.

Rapid and sensitive detection of trace amounts of analyte is still challenge in explosive analysis. This presentation will underline SERS based fast, sensitive and selective sensor regarding the most suitable active surface preparation techniques. The new labelled and label-free applications of Raman spectroscopy for the detection of targeted analyte such as ammonium nitrate are the main topics of this talk. The optimization strategies and the analytical performance of the SERS-based assays will be presented.

Keywords: labeled SERS, label-free SERS, nanoparticles, explosive detection

IL-8

The Preparation of Hydrazines Revisited

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A convenient and rapid synthesis of hydrazine was achieved by implementing a variant of the classic urea-hypochlorite process. The technology was applicable to batch & continuous flow syntheses. The approach featured desirable traits such as minimal start-up & operating costs, design & operational simplicity, high process safety, good yields, near-stoichiometric use of starting materials, rapid turnover & zero stabilizer/catalyst requirement.[1] The technology distinguished itself from ALL previously described synthetic methods in the sense that external energy was NOT required to synthesize hydrazine. The approach also served to prepare the hypergolic fuels methyl & 1,1-dimethyl hydrazine by reacting methylurea & 1,1-dimethyl-urea in place of urea. By way of this approach, it follows to reason that hydrazines may be locally & cost-effectively prepared upon demand at the small-to-medium production scale.[2]

The approach was implemented in a vigorously-stirred vessel or a continuous tubular reactor configured to prompt effective passive mixing. Aqueous alkaline urea & sodium hypochlorite were rapidly combined at ambient temperature, initiating reaction. An exothermic process quickly ran its course, during which time the corresponding hydrazine free base formed *in situ*. The synthesis appeared escalatable to practically all volumes, as it was not prone to thermal runaway. Excellent yields were obtained without the use of external heating/chilling, purified water, and metal-ion chelators[3] or co-precipitants.[4] Ground water was utilized as a coolant during the workup if hydrazinium precipitates were targeted. Alternatively, the free base could be distilled or a ketazine adduct decanted. While waste water was potentially recy-clable, it was more conveniently utilized by local industry in aqueous reduction processes.

In examining the upper limits of yield, attention was drawn to the urea-hypochlorite mechanism, which had been reported to reflect weight-averaged contributions of the Hofmann and Favorskii-type rearrangements. While the contribution of the Hofmann mechanism towards yield is undeniable and self-consistent within the literature, controversies concerning the true contribution of the parallel-running Favorskii-type mechanism have remained. Here, the role of the latter pathway was highlighted using 1,3-dimethylurea as starting material. The necessity of the carbonyl oxygen was also confirmed, as reaction using thiourea in place of urea again prompted an exotherm, but this time, neither gas nor hydrazine was produced.
Keywords: hydrazine, methylhydrazine, dimethylhydrazine, urea-hypochlorite, synthesis, preparation

[1]Most urea-hypochlorite processes use a significant excess of one or more reagents and longer reaction times. The remaining variants employ comparable but not shorter reaction times. Almost all previous urea-hypochlorite processes employ external cooling to lower the pre-reaction medium to sub-ambient temperatures, and all prior urea-hypochlorite processes employ external heating to rapidly raise the temperature of the reaction medium. All other known approaches to synthesize hydrazine also apply external heating and/or cooling at some point.

[2]The urea-hypochlorite variant herein is clearly advantageous compared to prior cases. Other established approaches have substantial startup costs compared to urea-hypochlorite. The hydrazine may serve as starting material for hydrazinium salts, semicarbazide and its salts, various semicarbazones, hydrazodicarbonamide, azodicarbonamide, carbodihydrazide, and various azines and heterocycles. The hydrazines (parent and methyl) can be distilled, yielding more concentrated material.

[3]In previously established methods, metal-ion "deactivators" have proved crucial for obtaining good yields. Some chelators are gelatin, animal glue, casein, albumin, peptone, starch, and ethylenediaminetetraacetic acid ($2Na^+$ or $4Na^+$).

[4]Paralleling the previous footnote, metal-ion co-precipitants have also proved themselves to be crucial "deactivators". Some include manganous salts, magnesium hydroxide & aluminum ion and oxidizable metallic precursors of said co-precipitants.

IL-9

Explosive Analysis Method-Development Studies in the Institute of Forensic Sciences: Evolution of the Methods For Faster Analyses, Higher Recoveries

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The crowded areas in especially urban settings are under more threat from the point of terroristic attacks in recent years. The easiness of the construction of explosive devices makes the situation more problematic. Analysis in post-blast explosive residues are important in identifying the type of explosive, characterization of the explosive such as country of origin and manufacturer [1]. In the Institute of Forensic Sciences, fast and simple LC-MS/MS methods are developed using ESI and APCI, in soil matrix, which is the most common available samples encountered in the crime scenes.

The studies started with a method development study on the determination of PETN, RDX and HMX. A green method with minimum solvent use was achieved using one step 2 mL acetonitrile extraction and the validation was performed. The average recoveries were between 76.52-84.77%, the method was environmentally friendly, fast and quite sensitive with low LOD and LOQ values as: 3.4-8.5 ngg^{-1} and 6.0-10.0 ngg^{-1}, in order.

Another sample preparation and chromatographic method was developed for TNT, RDX and HMX determination in soil, using a different extraction and chromatographic elution procedure. This time a more effective extraction procedure was developed with acetone use, for the explosives. Higher recoveries between 96.9-100.4 % were obtained. LOD and LOQ values obtained from the analysis of the spiked soils were 4.3-6.8 ngg^{-1} and 7.00 -10.0 ngg^{-1} for RDX and HMX, and 18.9 and 38.0 ngg^{-1} for TNT.

For taking a better step, more explosives were targeted for simultaneous analysis in soil. An LC–APCI–MS/MS screening method was developed to determine the trace amounts of TNT, RDX, HMX, PETN, TETRYL, picric acid, 2,6-DNT and TMETN which contaminate the soil after explosion. In the literature, studies regarding multiple explosive analyses with LC–MS/MS in soil are limited. To determine TMETN in the presence of RDX, HMX, PA, TNT, TETRYL 2,6-DNT and PETN in one run was challenging and a different technique was used to achieve this separation. Since it was hard to observe the specific primary and secondary ions for all the above-mentioned explosives in one run, no satisfactory simultaneous analysis method existed in literature for these explosives in soil. An extraordinary a gradient approach in MS/MS gas temperatures, successfully provided a selective LC-MS/MS elution after a single-step extraction with acidified acetonitrile. Recoveries were between 93.01-104.20%, with LOD and LOQ values between 8.9–161.2 and 13.2–241.5 ngg^{-1}. The elution time did not exceed 10 minutes as in the former ones.

The studies are going on for presenting fast LC-MSMS methods to the literature, with wider spectrum of energetic molecules in more number of matrices. The future studies under the light of the information obtained from the recent experiences, are planned to be carried out in various matrices with higher number of explosives in order to catch the molecules exist in the post-blast debris in one run.

Keywords: Nitro and nitramine based explosives, determination in soil, LC-MS/MS, RDX, HMX

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IL-10

New Generation Energetic Materials as A Force Multiplier

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IL-11

Evaluation of Network and Mechanical Characteristics of Composite Rocket Propellants Related with Corresponding Dynamic Mechanical Analysis

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Hydroxyl-terminated poly (butadiene) (HTPB) as binder, ammonium perchlorate (AP) and aluminum (Al) as solid fillers are the main ingredients for composite rocket propellants (CRPs) used in rocket engines. Since adhesion of filler particles and polymeric matrix directly affects the mechanical properties of CRPs, the content and nature of ingredients are vital to develop efficient solid propellants according to desired purpose. The focus was on the effect of important ingredients like isocyanates, plasticizer and bonding agent incorporated into the different propellant formulations. Dynamic mechanical analysis (DMA) is a powerful technique for characterization of elastomers over a wide range of temperatures that is possible to determine the storage modulus, loss modulus, loss factor and glass transition temperature for each propellant samples. The parameters obtained by DMA have been correlated with the results of mechanical uniaxial tensile tests as a mechanical characteristic and crosslink density as a network characteristic of the tested propellants.

Dioctyl adipate (DOA) was used as a plasticizer in the desired propellant formulation. A good plasticizer is needed to show important characteristics like a low glass transition temperature [1]. It means that plasticizer has impact on adjustment of different mechanical behavior depending on desired rocket engine design.

Moreover, different content of aziridinyl type bonding agents have been used to investigate effect on propellant characteristics. They have a big role to produce interaction between oxidizer and polymeric binder in terms of adsorption and attraction forces because binder-filler interactions can be enhanced using surface active agents known as bonding agents. The interaction between bonding agent and oxidizer particles produces either primary or secondary bonds [2]. Several suggestion of the undefined reaction mechanism of the bonding agent and the oxidizer particles can be made using their DMA curves.

In the last study, propellant network and mechanical characteristics were studied using propellant samples cured with three different diisocyanate containing curing agents. Diisocyanate residues produce rigid or hard segments in polyurethane network affecting network properties of CRPs [3]. Structure of diisocyanate agents are directly related to DMA characteristics of the propellants. Secondary bond formation of the related propellants caused by using different curing mechanism differ the properties of CRPs.

Keywords: Propellants, DMA, Plasticizer, Polyurethane, Diisocyanate

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IL-12

Development of domestic alloys for use in defense industry applications

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Aluminium and magnesium alloys are frequently used materials for automotive and aerospace applications due to their low weight and high strength ratios. Their high corrosion resistance makes these alloys very attractive choice of materials. The density of these alloys are more than one third of iron and steel; and mechanical properties can be enhanced easily by alloying or heat treatment. Lower section thickness and increased mechanical properties have become the focal point of study for these alloy groups. For domestication purposes, new alloys were developed to be used in unmanned air vehicle, helicopter and fighter planes.

IL-13

The Uses of Explosives in Civil Purposes: Some Case Studies

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Explosives can be classified into two groups as military and civil explosives depending on their intended use. Civil Explosives are used in many areas, especially in mining and construction industries.

During the use of the explosives, it is necessary to utilize the energy of the explosives, optimally. For this purpose, it is possible to control and minimize undesirable environmental impacts such as noise and air shock, vibration, fly rock by making appropriate drilling and blasting designs. For this reason, engineering science and technology in blasting operations should be used in accordance with the expected results.

In this study, the chemistry of the explosives is not mentioned. The applications, which can be given as examples of the use of explosive materials produced for civilian purposes for the purpose of serving people and results of these applications are given, briefly. In accordance with this aim, first, blasting for civil purposes and blasting result outputs are briefly mentioned. Then, application examples carried out in Turkey such as building demolition with controlled blasting in the city, demolition of two bridges by controlled blasting on TEM highway in Gebze district, the foundation excavation blasting carried out in urban areas and blast excavation works in tunnels opened under the settlements were briefly mentioned.

Keywords: Civil Explosives, Blasting, Urban Area

IL-14

Recent Development in Thermoelectric Materials, Thermoelectric Application from Space to Military

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Thermoelectric (TE) materials have attracted great attention recently due to their potential application for converting wasted heat, which is almost 60% of energy use in all world, into the useful electrical power, and local cooling. TE materials capable of converting heat directly into the useful electrical power or vise verse. Due to their unique properties, they are currently using in many industries such as electronic, medical, automotive, space and military as power generator or cooler. In spite of their many advantages such as no moving part, scalability and high reliability, they currently have relatively low efficiency. The efficiency of a TE device is depending on Z parameter that is characterized with three physical parameter, such as electrical conductivity, Seebeck coefficient and thermal conductivity. In the past decade years, a great effort has been conducted on developing high efficient thermoelectric materials and also on discovering their new potential applications. In this talk, I will give a brief information about thermoelectric technology and recent development on TE materials, current and future application fields especially in military and space industries. And then finally, I will give a brief information about current TE technology related research projects on going in our research group.

Oral Presentation

OP-1

Binder Dependent Cycling Performance Comparison of Different Anodes for Lithium Ion Batteries

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Lithium-ion batteries are a popular type of rechargeable batteries used in portable electronics and electric or hybrid cars [1]. The LIBs have advantages with their excellent properties such as no memory effect, large voltage range, low self-discharge and high energy density. However, the present LIBs have developments to increase the energy density, still several challenges are needed to be resolved prior to their applications in EVs [2]. These challenges include energy and power densities, cycle life, charge-discharge rates, safety and cost of LIBs [3]. Most of these challenges are related to electrode materials. Therefore, new material compositions with new electrode designs have the serious potential to improve the energy per weight and volume at reduced cost.

Present commercial anodes are graphite for LIBs. But limited energy density of graphite makes high capacity Si based materials an alternative electrode material. When the theoretical capacity of graphite, 372 mAh/g, is compared to Si based anode electrodes, 4200 mAh/g, it seen that Si based anodes have 11 times higher capacity than graphite. However, Si based anodes have some challenges which need to be overcome. The most important one is the volume change of Si (300% volume change) at the charge and discharge steps. As the result of this volumetric change, anode material has cracks, electrical conductivity is failed, ionic transfer, and the capacity decreases.

In this study, silicon and graphite were used as anode active materials with different polymer binders such as PVDF, PAA and PVA. The structure of the electrodes were analysed under SEM. Silicon and graphite electrodes were assembled as coin cell and the lithium were used as the reference electrode. Electrochemical analysis were performed resulting as cycle-capacity and voltage-capacity performance for 100 cycles. This study showed that performance of anode material for LIBs was substantially electrode composition dependent.

Keywords: anode, silicon, graphite, lithium ion battery.

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Poster Presentation

PP-1

A Superexplosive: Octanitrocubane

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Persistent endeavors have been made to grow new energetic materials having good thermal stability, impact and shock insensitivity, better performance, economic and green syntheses, to meet the future requirements of military and space applications [1]. High explosives have a powerful exothermic reactivity, which are attractive for both military and business applications [2]. The approach and utilization of green energetic materials to acquire ever more elevated energy and decreased vulnerability, enhanced mechanical properties along with reduced signature profile and extended useful life carries high significance nowadays [3].
Various nitro compounds are utilized as military and business explosives, fuels and propellants [4]: More powerful and less shock-sensitive derivatives are searched. Most of the attention is centered on high-density organic compounds which contain all of the elements needed for combustion to gaseous products in the absence of air. Energetic materials with the strained rings and cages as nitrocubanes are a promising new class of explosives [4, 5]. From these strained cages, octanitrocubane (ONC) and heptanitrocubane are the most powerful non-nuclear high-energetics currently known [6]. ONC is a cubane derivative with stressed rings and cages, with a high nitrogen content and high density between 1.98 - 2.06 g/cm^3, varying according to the nitro group orientation. Being shock insensitive, it provides a safer handling [6]. To our information, ONC is the densest explosive known with its highest detonation velocity (more power), and highest maximum detonation pressure. It is regarded as the best high-energetic material because of its velocity of combustion, not because of its specific enthalpy of combustion
Since ONC has no hydrogen, no H_2O forms when it burns; it leaves little or no visible smoke behind the rocket and these "low-signature" rockets will be difficult to track [4]. It has much higher energetic performance than RDX and HMX [7]. However, as a disadvantage, it has a complicated multisteps synthesis, starting from cubane monocarboxylic acid [4, 8]. Its synthesis and characterization was performed by Eaten et al. in 2002, however there is no information if a batch-synthesis has been made recently, whether it is used already by the military, as well as no trade of it seems to be carried out by any manufacturer. Because of the tracking or the analysis in post-blast debris will be more difficult than other explosive residues, this will be a challenging issue for the analytical chemists.

Keywords: Nitrocubane derivative, octanitrocubane, high density energetic material, powerful explosive, nitro derivative, new explosive

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PP-2

Production of RHA Reinforced Aluminum Matrix Composites

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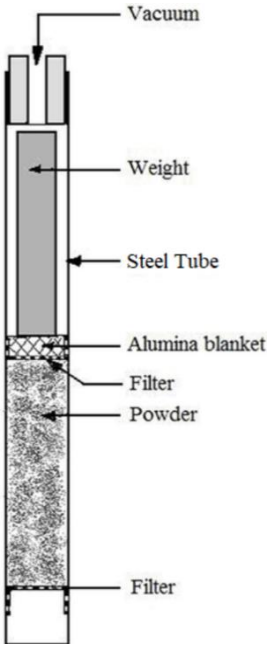
Aluminum matrix composites have begun to attract great interest in the industry thanks to the combination of high hardness, high strength, low weight and high wear resistance (1). Agricultural wastes are not used, they are accumulated in garbages, roadsides and waterways, or burned open air. However, by burning these wastes, methane and CO_2 gas is released into the atmosphere. With re-use processes, air pollution due to ashes and gases can be reduced (2). Many environmentally friendly agro-wastes are used as reinforcing fillers in developing composites. One of these many waste products, Rice husk ash (RHA) is an agricultural waste by-product plentifully available (3).

In this study, Al 7075 (89.9% Al, 5.6% Zn, 2.6% Mg, 1.6% Cu, and 2.6% Cr) matrix RHA (6.78% C, 56.40% O, 35.74% Si, 0.43% Mg, and 0.66% Ca) reinforced composites, having 1%, 2%, and 4% reinforcement-volume ratios, were produced by the vacuum infiltration method. RHA powders with the particle size of 30-40 μm were used as the reinforcement.



Infiltration tests have been carried out with steel tube shown in Figure with 10 mm outside diameter, 1 mm wall thickness and 300 mm length. Stainless steel filter was placed at the bottom of tube and on the filter an Al foil was placed to prevent spillage of powders. RHA powders were filled into tube to form 70 mm height freely. The melted aluminum alloy was kept constant at 750 °C ± 5. 500 ± 5 mmHg vacuum was applied to the tube and the steel tube was sunk into liquid aluminum. Vacuum was kept under these conditions for 3 min. After 3 minute vacuuming, the tubes were taken out.

Ratio	0%	1%	2%	4%
Porosity (%)	2,7483	4,3237	11,9238	13,2544
Hardness(HV)	102	111	109	105

RHA reinforced Al7075 matrix composites were produced by vacuum infiltration method. Composites were then solution heat treated at 485 °C for 2 h and aging heat treated at 120 °C for 24 h. Microstructural investigation and hardness tests revealed that while porosity of composites increased with increasing RHA content, hardness of composites decreased and heat treatment has not any significant effect on the properties of composites due to the pores formed and expanded during T6 process. It was found that porosity in composites increased with increasing RHA volume fraction. Additionally, increasing RHA volume fraction in composites caused to decrease the hardness of composites. This situation was triggered by porous structure of RHA.

Keywords: aluminium, RHA, infitration, composite, vacuum

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PP-3

PPy Based Anode Binder for Lithium Ion Battery Application

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Many of systems from electronics to electric cars use energy storage systems which must have high energy and power densities with cost efficiency [1, 2]. Lead acid, nickel metal hydroxide and other batteries have been used as traditional energy storage devices. In the last 20 years, due to the advantages such as high specific capacity, high coulombic efficiency, long cycle life, high energy density, no memory effect and high operational voltage of the LIBs, they have achieved great success in consumer electronics and electric vehicles [3]. Generally, graphite has been used as anode active material in Li- ion battery (LIB) because of its good cycle life and low stable discharge voltage plateau [4]. The specific capacity of commercial graphite anode, 372 mAh/g, however limited energy and power density which decreases the application of it in electrical vehicles [5]. Therefore, nowadays new anode active materials have been started to develop. The highest theoretical gravimetric capacity (4200mAh/g) of silicon (Si) is nearly ten times higher than graphite [6]. But, Si-based anodes have limited application in LIB due to the loss of contact with current collector because of large volume change during lithation and delithation processes. To overcome this problem, porous and conductive polymers were used for improving the chemical composition and the mechanical strength tolerance of Si anode. In this study, conductive colloidal polypyrrole (Col-PPy) which synthesized with oxidative chemical polymerization of pyrrole (Py) by cerium ammonium nitrate (CAN) in N,N'-dimethylformamide (DMF) was used as polymeric binder in Si-anode (Si/Col-PPy) to overcome the electrical conductivity problems during the volume change. Col-PPy solution was used alone and together with polyvinylidenefluoride (PVDF) and polyvinylpyrrolidone (PVP) in order to improve the cyclability and capacity of Si-anodes. These Si-anodes were further analysed with cycle tests and combined cycle tests at different rates (C-rate) in half cell and SEM images of electrodes were taken before and after cycling.
High reversible capacity (2617 mAh/g at C/10 (0.42 A/g)) and good cycling performance (reversible capacity of 1400 mAh/g after 189 cycles at C/3 (1.4 A/g)) were obtained from Si/Col-PPy anode for LIB.

Keywords: Lithium ion battery, silicon anode, conductive polymer, colloidal, polypyrrole

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PP-4

Graphene Based Electrodes for Iron Redox Flow Batteries

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Redox flow batteries are taken great attention due to their advantages such as great energy efficiency (up to 80%), flexible design, long cyclic life, simple control and monitoring system, low maintenance cost, and eco-friendly structure.[1-3] Iron based flow battery is a type of the flow batteries. Electrode materials play key role in this type of battery for the performance of the battery.[4] Although graphite-based electrodes can be used as electrode materials in the battery system, novel electrode components can improve the performance of the battery.

In this study, graphene-based electrodes were prepared and used as electrode materials of the iron flow battery. The electrodes were characterized by cyclic voltammetric (CV) and electrochemical impedance spectroscopic (EIS) methods. In cyclic voltammetric analysis, currents and capacities of anodic and cathodic peaks were investigated. Solution resistance, charge transfer resistance and Warburg impedance values were determined in EIS analysis. The surface morphology of the electrodes was also investigated by using of scanning electron microscopy.

Keywords : Graphene Electrode, Electrochemistry, Cyclic Voltammetry, Redox Flow Battery, Energy

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PP-5

Electrochemical Determination of TNT and DNT with Gold Nanoparticles/Poly(Carbazole-Aniline) Film−Modified Glassy Carbon Sensor Electrodes Imprinted for Molecular Recognition of Nitroaromatics

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The relatively heterogeneous distribution of explosives in contaminated and remediated land make field analysis techniques extremely important in exploring the nature and distribution of these contaminants. Although the highly sophisticated current techniques for detecting/quantifying trace explosives include ion mobility spectrometry (IMS) and gas-liquid chromatography (GLC) equipped with mass spectrometry (MS); most of these devices are expensive, and require qualified personnel and time-consuming procedures [1]. As an alternative to these methods, electrochemical methods are preferable because of their high sensitivity and selectivity, fast response, low cost, easy operation, and portability [2].

In this work, a novel electrochemical sensor was designed for detecting nitroaromatic-type energetic materials (2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT)), relying on gold nanoparticles (Au_{nano}), modified glassy carbon (GC) electrode coated with nitro energetic memory−poly(carbazole-aniline) copolymer (Cz-co- ANI) film (e.g., TNT memory−GC/P(Cz-co-ANI)-Au_{nano} modified electrode). These sensor electrodes were prepared in two steps. In the first step, GC working electrodes were coated with the target energetic material (template) and carbazole-aniline monomers using electrochemical polymerization. TNT and DNT were used as template molecules. After this step, the surface of the energetic material memory−copolymer electrode was functionalized with gold nanoparticles. TNT memory−GC/P(Cz-co-ANI)-Au_{nano} modified electrode for TNT determination and DNT memory−GC/P(Cz-co-ANI)-Aunano modified electrode for DNT were used as sensor electrodes. Current was recorded against concentration to build the calibration curves that were found to be linear within the range of 100−1000 μg L^{-1} for 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) by using square wave voltammetry. The corresponding limits of detection were 25 μg L^{-1} for TNT and 30 μg L^{-1} for DNT. These electrodes were used separately, and specific determinations were made in various mixtures of nitroaromatic energetic materials [3].

The developed voltammetric method and sensor electrodes are assumed to be useful for determining the shelf life of military ammunition containing nitroaromatic energetic materials and also for field detection of explosive residues or for measuring the treatment levels of remediated land after military use.

Keywords: Nitroaromatics, sensor electrode, molecular imprinted polymer, gold nanoparticles.

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PP-6

Gas Chromatography-Mass Spectrometric Detection of Triacetone Triperoxide (TATP) Based on Solid Phase Extraction

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Determination of triacetone triperoxide has gained importance in recent years due to some historical terrorist actions such as 2005 London Subway bombing, 2009 failed terrorist attempt in a Northwest Airways flight, and Paris suicide bombing in 2015[1]. TATP detection represents a serious challenge because conventional explosive detection devices used for airport security rely on the presence of nitro groups or metallic elements for a positive response[2]. Due to its high vapor pressure, TATP can be analyzed with air sampling techniques. In this study, TATP was synthesized according to the literature[3] and detected using solid phase extraction (SPE)-based gas chromatography-mass spectrometry. The system which was designed for TATP is based on extracting TATP from a matrix media by exploiting its sublimation properties. A known amount of TATP sample in a watch glass was placed into SPE apparatus. The collecting TATP vapor into a column (LiChrolut EN) was eluted and then injected to the GC–MS system.

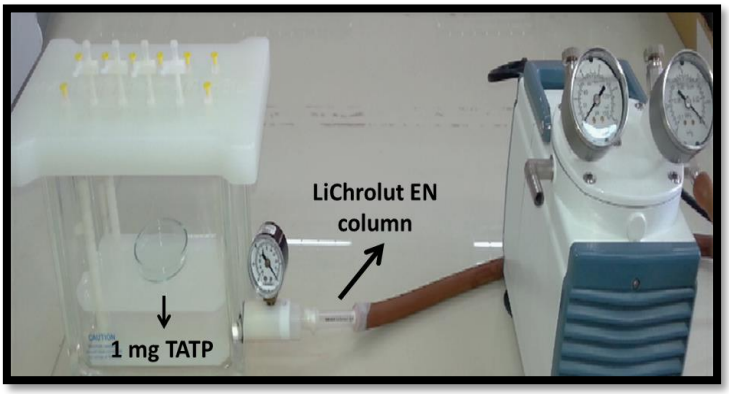

Figure 1. The designed SPE system for TATP sample.

Keywords: Solid phase extraction (SPE), triacetone triperoxide (TATP), gas chromatography–mass spectrometry (GC–MS)

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PP-7

Indirect Colorimetric Sensing of Home-Made Explosives (TATP & HMTD) using Tetramethylbenzidine Reagent

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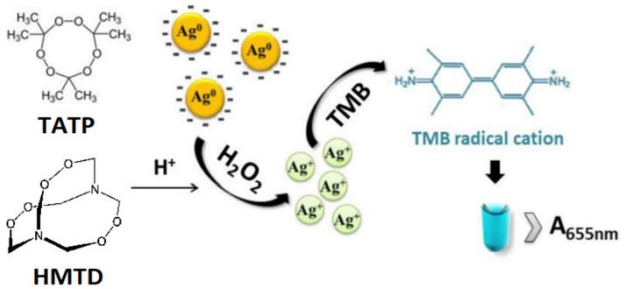
Hydrogen peroxide (H_2O_2) is a synthetic precursor and degradation product of home-made explosives, such as TATP and HMTD.[1] Due to some historical terrorist actions, determination of home-made explosives (*i.e.*, peroxide explosives) at trace levels has gained importance in recent years.[2] The two members of home-made explosives, triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD), can be manufactured from readily accessible reagents, and are difficult to detect by conventional analytical methods.[3] Colorimetric determination of TATP and HMTD is greatly facilitated when it is hydrolyzed to H_2O_2. In this respect, a selective, sensitive, cost-efficient and easy-to-use colorimetric sensor was developed for indirect determination of peroxide-based explosives which are lack of chromogenic/fluorogenic functional groups. Detection principle of the developed sensor is that TATP and/or HMTD is hydrolyzed to H_2O_2, which partly oxidizes silver nanoparticles (Ag^0NPs) to Ag^+, which in turn oxidizes an auxiliary probe, TMB (3,3′,5,5′-tetramethylbenzidine), to the blue-colored diimine. Indirect colorimetric determination of H_2O_2 is made by absorbance measurement at 655 nm, characteristic to the oxidation product of TMB. The hydrolytic degradation of TATP and/or HMTD to H_2O_2 was performed using a strongly acidic cation exchanger resin Amberlyst®-15. The responses of detergents, sweeteners, acetylsalicylic acid (aspirin) and paracetamol-based painkiller drugs, which may be used as camouflage material in passenger belongings, were also examined.



Scheme 1. Schematic presentation of the developed colorimetric sensor for TATP and HMTD determination.

Keywords: Silver nanoparticles (AgNPs), home-made explosives, colorimetry, TATP, HMTD

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PP-8

Determination of Propellant Energetic Material Ammonium Perchlorate with Spectroscopic Sensor

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Ammonium perchlorate (AP) used in solid rocket propellants is the most commonly used oxidizer of composite solid propellants [1]. The ammonium perchlorate has a ratio of 70% by weight. Thus, it is the main component of a fuel. It is also oxidizing because the oxygen content is 54.5% by weight. In rocket production, the increase in the use of ammonium perchlorate suggests that ammonium perchlorate is a good solid oxidizer [2]. Ammonium perchlorate (AP) is one of the most widely used, yet probably least understood energetic materials. Over the past several decades, numerous papers have been devoted to the decomposition mechanism and structural properties of AP [1]. Nanostructured materials are playing an increasingly important role in scientific research day by day. The physical and chemical properties of these materials are undergoing tremendous changes when their size is reduced to nanometers. Hence, we developed a sensitive, cost-effective and easy-to-use sensor in conventional laboratories for the naked eye determination of AP which based on changing size of the modified gold nanoparticles interacting with ammonium perchlorate. The proposed assay was optimized with respect to a number of parameters such as the mode of preparation of gold NPs, concentration of dye, modification time, etc. The linear calibration equation of the developed method for AP was: $A_{620/520}=5.22\times10^{2}\ C_{AP} - 1.62\times10^{-2}$ with a correlation coefficient of r = 0.9926. The analytical performance characteristics of the developed sensor for AP as molar absorptivity (ε); limit of detection (LOD) and limit of quantification (LOQ) are as follows: For AP, $\varepsilon= 712\ L\ mol^{-1}cm^{-1}$; $LOD= 2.4\times10^{-5}\ mol\ L^{-1}$ and $LOQ=8.33\times10^{-5}\ mol\ L^{-1}$. Additionally the interference effects of various anions and cations commonly found in soil such as Cl^-, NO_3^-, K^+, Mg^{2+} and Ca^{2+} were investigated. The developed quantitation method was statistically compared with the extractive spectrophotometric method in the literature using t- and F- tests.

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PP-9

Development of Spectrofotometric Method for Energetic Material Ammonium Dinitramide Determination

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Ammonium dinitramide (ADN) is a powerful, environmental-friendly oxidizer developed in 1990s for use in composite solid rocked propellants [1]. ADN has emerged as interesting candidate for replacing AP (Ammonium Perchlorate) as a halogen free oxidizer in composite propellants. It also a large potential as an ingredient in gun propellants, as well as for underwater explosive applications [2]. Nanotechnology, and alongside nanostructured materials are inroduced to the market. If the dimensions of the chemical properties approach the nanoscale, tremendous changes of the physical, but also electrode (GMGCE) was developed to investigate the electro reduction of ammonium dinitramide (ADN) using cyclic voltammetry and differential pulse voltametry techniques [3]. There are very few methods of determination for energetic material ADN. Furthermore, there is no colorimetric sensor capable of determinining amount of ADN in a mixture of nitroaromatic and nitramine energetic materials. In this regard, the aim of this works is the ADN determination. In this study, spectrophotometric determination method for ADN has been developed with the aid of modified gold nanoparticles [4,5]. Detection principle of the sensor is the determine the hydrolysis product of ADN with modified gold nanoparticles. The linear calibration equation of the developed method for ADN was: $A=2.33\times10^{-2}\ C_{ADN} + 5.55\times10^{-2}$ with a correlation coefficent of r = 0.9990. The sensor was applied to energetic materials mixtures containing nitroaromatics and nitramines. The possible interference effects of various anions and cations commonly found in soil such as Cl^-, NO_3^-, SO_4^{-2}, Mg^{2+}, $Ca^{2+}$and K^+were studied. Additionally the effects of detergents, sugar, sweeteners, acetysalicylic acid (aspirine), caffeine and paracetamol-based painkiller drugs, which are used as camouflage passenger belongings while carrying the explosives, were examined.

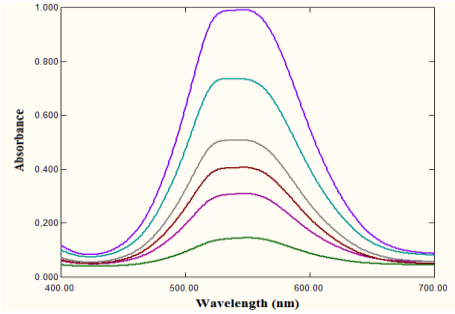

Figure 3. Calibration spectra of NO_2-(generated from ADN) with 4-ATP-AuNP+NED method.

Keywords: Ammonium dinitramide, spectroscopy, nanochemistry, rocket propellant.

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