Modern Analytical Chemistry Methods for Chalcogen Materials Analysis and Characterization

Surjani Wonorahardjo, Fariati Fariati and
I Wayan Dasna

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.77989

Abstract

Analytical methods are needed to elucidate modern and complex compounds as well as to describe their physical properties. The underlying principles of chalcogen chemistry as well as the natural abundance of chalcogen elements are the base of building many biological substances, including sophisticated materials for future applications. Thus, the need for modern and state-of-the art analytical methods and techniques to characterize them, is obvious. In this chapter, challenges in analytical methods for chalcogen compounds and materials, as well as some examples of natural or synthesized materials or their combinations, including biomaterials, are discussed. Modern methods for chalcogen compounds analysis and structural determination discussed include: UV-Visible and infrared spectroscopy (UV-Vis and IR), thermo analysis, electrochemistry, magnetic analysis, chromatography, X-ray methods (mostly XRF, XRD, and EDX), high-resolution microscopy (SEM and TEM), multinuclear NMR, computational analysis, and bioassay. Also, the historical background and nature of chalcogen elements, including reactivity and magnetic properties as well as thermal behavior, common compounds of chalcogen elements: organic and inorganic materials, complex chalcogen materials, will be briefly discussed.

Keywords: analytical methods, chalcogen materials, characterization, application

1. Introduction

People living in this scientific era might not realize that chalcogen elements are everywhere in our lives. Especially oxygen which is essential for living, and then sulfur and selenium which are so close to the human life, as they are incorporated or form parts of essential and useful compounds and materials. Tellurium and polonium might not be inbound to life, but they are utilized for some purposes according to the new properties and attributes of material, as nanoselenium with their high active surface area and catalytic efficiency [1, 2]. The interest for chalcogen materials is growing rapidly, as seen through SCIFinder [3]. Combinations with other elements make the compounds important for metabolism or for various dedications. The investigation on possibilities of chalcogen elements in reaction has been thoroughly discussed from the internal chemical properties of the elements [4]. Availability of pair and lone-pair electrons offers so many possibilities of combination, naturally and synthetically. There has also been a description of the stability of organo-chalcogen compounds by intermolecular coordination because of their role in chiral induction [5].

Secondary metabolites and study on metabolomics have dominated the area of biology, food, agriculture, and also medicine, as well as pharmacy. One good example, is the chemistry of garlic, in which the sulfur-containing compounds called Allicin dominated the most beneficial properties of garlic as an antioxidant, antimicrobial and antifungal actions [6]. More similar analysis on *Allium* family revealed that mostly sulfur compounds were responsible for the antioxidant and antimicrobial properties [7]. The phytochemical profiles describe the benefits of sulfur-containing compounds to the good bioproperties which have good prospect in the future. Besides sulfur, selenium plays a preponderant role in cellular metabolism and becomes an essential element in enzyme in protecting the body against oxidative damage as well as many other functions [1]. Selenium is needed in life in certain amount; otherwise, it can be toxic, as sometimes it is called by double-edged sword element [8]. This element is also being well investigated by scientists in relation with its bioavailability in the environment [1, 2]. Originally, selenium is present in rocks, water, and soil, and it has some common isotopes too [9], though it naturally occurs in biological cycles in the environment, including the biochemical and food cycles. Selenium is one of the metalloid essential minerals in living things, whereby its deficiency, in soil and crops can cause certain metabolic disease such as the Kashin-Beck disease, commonly prevalent in the Tibetan plateau [10]. In short, the exploration of chalcogen elements contained in natural compounds as minerals is still intensive worldwide, while a shift toward agricultural use is currently underway [1, 9, 11].

The new materials in combination with metals and ligands with higher specification and sophisticated preparation are in demand due to great contribution for modern technology. Selenium, for example, can be immobilized through reaction to form selenium metal-humic ternary complexes or incorporated in carbohydrates as well [9]. More related to life, thio-compounds cannot be uncounted for since they are all over the synthetically chemicals through the ligands or thiolates as well as selenolates [12]. Synthetic compounds with metals like Fe by chalcogen arsenide [13] or chalcogen containing iron-carbonyl clusters [14] are already done. Chalcogen elements as dopant in silicon layers [15] or as organo-selenium or tellurium cations [16] are also analyzed by spectroscopy methods. Tellurium is a bigger chalcogen element and tends to have isotopic abundance, from which some are stable and some unstable [17].

There are several reports on chalcogen material synthesis with various synthetic and analytical methods, available in the Handbook of Chalcogen Chemistry [3]; however, with the emergence of new and complex compounds, analytical methods development is undoubtedly becoming an endless effort in the field of chalcogen chemistry. How the new materials are

http://dx.doi.org/10.5772/intechopen.77989

explored and investigated and also how the applications are being established and confirmed are both the new challenges of analytical chemistry. In the future, the chalcogen materials cannot be discussed within the scope of chemistry only, but must be broaden in the context of science in a more general knowledge.

2. Nature of chalcogen compounds and chalcogen materials

Chalcogens are elements which belong to the group VI-A (or group 16) in the periodic table, which consists of oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and polonium (Po). Chalcogens are the basic elements of chalcogenides compounds, where chalcogens are combined with electropositive elements, organic radicals, in natural secondary metabolites and even in macromolecules such as enzymes and proteins [1, 18, 19]. All compounds with oxygen can be essentials and contribute most of the chalcogen materials. The materials can be as simple as silica, as an example of oxygen compounds was made for some important application [20] or macromolecule like cellulose or its derivates [21] which is applicable in daily life and will be so still in the future, to a more complicated complexed compounds [22–26] or advanced materials [27–29] which are made for the sake of science and method development. Abundant materials are naturally in existence with oxygen, and also a lot is being derived from synthesis in the laboratory [20–26, 30].

Some literature exclude oxygen from the chalcogenides discussion as oxygen appears in almost all materials [3]. Oxygen and sulfur are contained in so many secondary metabolites in living things and also in bigger molecules in tissue [6, 18, 31–34]. The process of changing compounds during food treatment enables one to establish new natural resources for modern herbal medicine for cancerous treatment [7, 35–39]. To be able to examine the biomolecular structure and medicinal properties of such compounds in detail, new analytical methods and also high-resolution instrumentation would play important roles [40–42]. Of course that pretreatment prior to analysis will be taken into account [31, 41, 43]. Extraction process which is needed before the analysis was discussed thoroughly in the prominent book of Harborne [44]. Many sophisticated new materials are made and dedicated for use in medicinal area [35, 38, 45] or smart electronic materials [46], materials from nonliving beings [3, 47, 48], nanomaterials and thin films and materials for certain applications which needs special characterizations [49, 50]. The fast development of chalcogen materials cannot be separated from the development of analytical methodologies.

3. Chalcogen bonds

Most topics on chalcogen compounds and materials are related to real chemical bonding, which are either ionic or covalent bonding in one molecular building. Fewer discussions describe the weak intermolecular forces that bind molecule or macromolecule together for certain purpose. Chalcogen bonds are important in many intermolecular interactions which in turn determine the configuration and designs of bigger biomolecules [51]. This type of bonding can be grouped as dipole–dipole interaction. In the field of biochemistry, it has much impact due to its role in bigger molecular mobility. The chalcogen bonds also form eclipse (*cis*) and staggered (*trans*) configurations, enable chalcogen elements to develop many types of materials for specific application, from real crystals to real amorphous substances.

The intra-molecular chalcogen bonds were obtained from the X-ray diffraction results and quantum chemical calculations, such as in thioindirubin [52], indicating advanced methodology in modern analysis of big molecules. Chalcogen bonds were also studied with the aid of computational programs, as the development of old theories, especially in the debates around the energetic significance and physicochemical origins of the so-called class σ-hole interaction [53], continue to fuel scientific discussions. These approaches have served as important steps toward the synthesis, analysis, and designing of new materials [51].

4. Challenges in analytical methods for chalcogen compounds and materials

Natural chalcogen compounds which are present in certain matrix in perfect blends, and separation procedure must be conducted first, followed by purification prior to analysis. There are several parameters must be taken into account for the correctness of measurements. In the extraction of sulfur-containing compounds in plants, one would normally use phytochemical procedures [44] by considering the separation of constituent analytes according to the similarities of the compounds.

The development of new materials from chalcogen compounds due to the functionality of the materials must be supported by a better analytical methodology. When materials are dedicated to a specific purpose, then the proof to that claim might be assigned analytically too. In this case, there are two types of analytical chemistry for the assignment of chalcogen materials. In short, the need of analytical method can cover four types of analysis:

1. The need of pretreatment method prior to analysis, for the natural compounds in natural matrix.
2. The need of methods for characterization of the chalcogen compounds, as well as new materials, in practice and theoretically.
3. The methods to describe the application for the new materials which include several other fields of disciplines.
4. The need of methods validation involving more than one method and instrumentation.

All of the human efforts in the laboratory as well as in computational analysis are based on the four types of analytical objectives listed above. The emphasis must depend on the purpose or in one segment of a longer process and all point of views can count. Therefore, any bigger steps can be started from chemistry discussion and developed into a wider investigation perspective.

5. Methods for chalcogen materials characterization

Characterization method is the backbone of chalcogen chemistry material description, as it always accompanies the explanation of material properties [54–57]. There are still some divisions in chalcogen material characterization, which includes the analysis for the main material itself and characterization of the impurities. The presence of impurities will decrease the quality to some extent [58, 59]. Notwithstanding, there have been too few reports discussing the impurities aspect if not related to their main functionalities.

Basic spectroscopy methods, especially X-ray methods, are the main tool for material characterization, including chalcogen materials. The methods are based on incoming X-ray beam that undergoes some natural phenomena like absorption, emission, fluorescence, and diffraction, then scattering with many possibilities to explore the chemical composition and properties of the sample. The crystallinity of materials can be derived from the X-ray diffraction patterns and the crystal database from instrument companies. In this case, the X-ray penetrates through the materials, and a number of particles can be expected to be oriented in such a way as to fulfill the Bragg's law. Almost all crystalline compounds analysis rely on XRD spectra, such as analysis of metal complexes of metal-thiourea and metal phenyl-thiourea [60, 61] after several steps of synthesis, to determine the coordination sphere on the metal Zn(II), Co(II) and Cu(II) and the possible crystal structures. More study of the spectra confirmed the shape of crystalline compounds together with UV-Visible and infrared as well as magnetic susceptibility measurement. In other synthesis the X-ray spectra were used to calculate reactive tendency as well as shape of molecules [23–25] besides characterization. Another X-ray technique is the energy dispersive analysis by X-rays (EDX) which intensity is proportional to the amount of the elements. The method is commonly combined with scanning electron microscopy (SEM) to get pre-experimental data, before the variables are given [22, 24, 26] or to characterize and give elemental confirmation [62].

Nuclear magnetic resonance for solid sample can be powerful to characterize chalcogen materials. It is based on the impact of radiofrequency irradiation on specific nuclei in certain field strength of the magnet (FT-NMR), causing the nuclei to spin resulting in resonance frequency which is an indication of the atom (e.g., ^{77}Se and ^{125}Te) [28]. NMR for chemist such as ^{1}H or ^{13}C NMR is usually the most important method for chemical structure elucidation. However, material scientists need solid-state NMR with its magic angle spinning (MAS). Moreover, when other nuclei of resonance are used, one must swing the magnetic field according to selected NMR active probe nuclei, such as ^{77}Se and ^{125}Te NMR [28, 29] to describe and confirm newly synthesized octahedral coordination compounds. NMR method assisted the description of how chalcogen elements (Se and Te) that can replace halogen as inner ligands in forming cluster cores in octahedral cluster complexes. This action reduces the symmetry and makes distortion on the metallic cluster as well as their isomers and of course changes the properties of the whole materials. Proton and (^{1}H) carbon (^{13}C) NMR of complex protein molecules were employed to investigate *Se*-(2-aminoalkyl)selenocysteines as biochemical redox agents [63]. In this case, chalcogen-biochemical substance was investigated through the behavior of its protons and carbons. The similar proton, carbon as well as ^{77}Se spectra recorded, was also the main method of metal chalcogenides characterization synthesized from single source molecular precursor, besides X-ray diffraction [64]. This NMR method extended to confirm the presence of chalcogen atoms in the complex molecular building through ^{195}Pt NMR. There was also a good NMR result which suggested the coordination of thiones to Zink(II) although the sulfur (S) atoms indicated an up-field shifting of = C=S resonance of ^{13}C NMR as well as a downfield N-H resonance in ^{1}H NMR [65]. Similar analysis was done for the characterization of complex coordination compound using thiourea derivative for biochemistry research purposes [66]. The proton NMR was also used to analyze the stability of intermolecular coordination as one good aspect is organo-chalcogen compound [5]. One can see that NMR is very useful in describing molecular properties and mobility.

Thermogravimetric analysis is a method in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate) or as a function of time (with constant temperature and mass loss). The important method of differential thermal analysis (DTA) one in which the mass changes is related to specific heat capacity. The increase of temperature is programmed to be linear and the heat flow to both sample and reference. Solid decomposition will occur due to phase changes, and this process can be endothermic or exothermic. One example of the methods on chalcogen compound was reported in the discussion of TGA of zinc and cadmium thiolate and selenolate complexes that showed the formation of metal sulfide (MS) and metal selenides (MSe) [M = Zn, Cd], while the mercury complexes showed complete weight loss in this temperature range [5]. TGA is mentioned as a good method to characterize metal chalcogenides [67] and has become a key analytical information generating technique together with X-ray diffraction data to validate the formation on chalcogen arsenide clusters in the iron with carbonyl functional groups [13]. In studying the degradation of palladium thiolate and selenolate, TGA was also used, to confirm the formation of Pd_4S and $Pd_{15}Se_{17}$ which was then characterized by XRD and EDX [64].

Optical microscopy is used after the synthesis steps of chalcogen materials, which aids the visual characterization of materials. This method is improved continuously and became the earlier stage of today's electron microscopy. Reflection mode of the instruments is preferable, and this method is called episcopic light differential interference contrast (DIC) microscopy, which enables imaging of polymer, glasses, semiconductor, metals and minerals sample with various reflective properties. DIC microscopy also has its limitation, as it gives experimental uncertainties during measurement, which is discussed in several numerical methods to minimize them [57].

Scanning electron microscopy (SEM), which is a technique used for a better description of materials' surface textures up to nanometer scale, is a good way of visualizing chemistry by secondary electrons. The ability to focus the extremely small incident wavelength of the energetic electrons to resolve object in extraordinary spatial resolution, makes the method popular for nanotechnology's purposes. Electrons are scattered very intensively compared to X-rays in both elastic and inelastic ways for both organic and inorganic materials, in dimensions less than 1 nm. While transmission electron microscopy (TEM) is a similar microscopy electron, but the image is formed from the passage of some electrons passing through thin sliced samples together with the elastic and inelastic scattering of the electrons. Thicker samples result in decreasing energy of the electron beams and increasing the scattering as well as complexity from the bigger distribution of energy and at the end declined resolution is obtained. Most of the synthetic chalcogen materials or metal chalcogenides are firstly being visualized with the aid of SEM and TEM before any other theoretical modeling or use of methods for analysis [15, 20, 24, 50, 56, 62, 68–70].

Dispersive infrared (IR) spectroscopy has been in use and became more popular with the modern nondispersive Fourier transform-infrared (FT-IR) systems to probe the presence of certain functional groups. From the energy point of view, vibrational frequencies are the base of most analyses, and rotational frequencies also count. Raman spectroscopy, on the other hand, from very different principles of spectroscopy, the scattered intensity of the absorbed energy informs the same energy absorbed by vibration. Sulfur is observable by infrared spectroscopy [66, 71, 72] by their vibrational modes, especially stretching and bending vibrational modes in solid, liquid, or gaseous phases. Fingerprint region is also important. Bulk characterization by IR was employed to analyze synthetic compounds to prove the presence of thionyl vibrational mode (ν(C-S)) with frequency band shifts to lower values after coordination with metallic atoms [66]. Similar recording of infrared spectra were found in metal complexes of thiourea and phenylthiourea crystals [60, 61]. The C-H stretching of the components overlapped with N-H stretching of the thiourea, but both can be differentiated since N-H is not directly involved in bond formation with the metals. The metal ion complexation on the ligands is more pronounced on N-C and C=S bond which is shifted after the complex is formed. It is also confirmed that the phenylthiourea is coordinated to metal *via* the sulfur with a reduction in π-electron density of the C=S bond.

Surface characterization modes use additional probes such as attenuated total reflectance (ATR) or diffuse reflectance infrared Fourier Transformed spectroscopy (DRIFT) [9] or reflection absorption infrared spectroscopy (RAIRS). Sorption study of selenium(IV) solution on natural zeolites was done by infrared spectroscopy [73]. In this case, pH and concentration of sodium selenite solution onto shabazite, analcime, stilbite, mesolite from volcanic fields were studied. Some new absorption bands from Se-O as well as Se-O-Se bridges were observed, different from original infrared spectra recorded before. The strongest changes due to the highest pH of sodium selenite were the shifted absorption of tetrahedral Al-Si-O of the natural zeolite framework downfield in alkaline situation and another band appeared that confirms the absorption state of the ions. The partial desilylation of zeolite in alkaline medium as well as dealumination of zeolites occurring in acidic solution were observed in the infrared spectrum. In thin film form materials, near infrared (NIR) analysis was used to compare the photo-response of silicon doped with Se and Te via laser irradiation [15]. In this case, surface morphology and optical properties were accessed by NIR spectroscopy, as well as the stability of Si-chalcogen interaction. In other discussion, the vibration-rotation spectrum informs the bond length of the molecules being investigated [71] and process chemistry can be followed. A very minute detail of absorption energy can be useful, making this method valuable from time to time during synthesis, for calculating and determining the crystal building of the structure. Moreover, some workers have used IR spectroscopy to complement the computational calculation of new inorganic complex cluster with chalcogen elements [29].

Most of organic and inorganic compound or ions adsorb radiation in the ultraviolet and visible region (UV-Vis) (180–750 nm). Part of chalcogen materials also produces electronic spectra that show shape of molecules or crystal as a result of the frequency absorption bands from ligands, especially for the bands near the visible region as expected [60, 61]. Furthermore, the electronic transition in *d*-orbitals also provides strong evidence for complex compounds containing transition metals. Examples of similar complex metal chalcogenides follow the same principles for different shapes of molecules, together with analysis of magnetic susceptibility, which suggests the shape of environment of the central metal ions with the presence of chalcogen ligands.

One other important analytical method for both characterization as well as application of chalcogen materials is electrochemistry [74]. The role of electrochemistry in synthesis, development, as well as characterization, up to applications, is obvious. This method is based on electron transfer in chemical reactions, in which metals have the most possible elements for electron storage systems. In photo-electrochemical systems, in which electron from the reaction is to be stored as energy or used for the next reaction.

Characterization of magnetic properties is also important in the study of chalcogen materials. Before, vibrating sample magnetometer was used to get information about the magnetization of samples when vibrated in a uniform magnetizing field. Magnetization is therefore induced, the product of magnetic susceptibility and the applied magnetic field provide chemical information of the materials. The specific techniques include: magnetic separation, magnetic spectroscopy, magnetic susceptibility measurement, magneto-relaxometry, magnetic particle spectroscopy, and rotating magnetic field. Some magnetic properties can be changed due to chalcogen substitution to metal iron complexed compounds [55, 75].

Dynamics in chalcogen materials is also trending in the field since it is crucial to describe the desired properties of the materials. In addition, the dynamics of materials are now core in understanding conductivity and diffusivity of the materials [76]. Materials with ion dynamics of different substructures enable phonon scattering process in their solid state. Actually, NMR relaxation and diffusion experiments are powerful tools used to describe molecular mobility, no matter what the nuclei probe is [77, 78]. The same method can be applied to characterize chalcogen materials as well as metal chalcogenides.

Since computer is involved in most of the modern chemical analysis, the chalcogen bonds in protein are one example in this field [79]. The computational analysis needs some unfamiliar tools and methods; however, it provides a lot of information about how molecules bind together naturally. Sulfur, selenium and tellurium are the probes of energetically favorable trends in the synthesis of chalcogen complex structures [29], following modeling by computational analysis. In addition, while there are more types of interaction occurring together in the biomolecules, which one cannot resolve them one by one, nonionic and noncovalent bonds are usually resolved by computational calculation. The intramolecular forces between sulfur and oxygen was also reported as the chalcogen bonds which is responsible for many bond formations in bigger molecules [52] is often being modeled by means of computation.

6. Methods for testing the applications of chalcogen materials

The method of applications will depend on the field of applications. The difficult part of it is to find a probe or indicator for the desired properties needed to be performed by the materials. This includes more analytical chemistry, with biological capacity or computer calculations. Suitable characterization is also essential to correlate the application and the properties of the materials.

Application of many types of chalcogen materials for environmental purposes employs infrared sensing for chalcogenides fibers [72] and also extended to other signal in infrared region can be utilized for environmental sensors. The manufacturing and testing of optical fiber sensors made from transparent chalcogen compounds for environmental can also be an alternative device for use in infrared spectroscopy [80].

For agricultural or medicinal application, bioassay is mostly used. New materials for antimicrobial properties are tested using qualitative or quantitative microbial assay [60, 61], in which pathogenic microbials were used to test the biological potentials of the compounds synthesized, as seen from disc diffusion method. The cultured microorganism in petri dishes would give clear inhibition zones around a spot of medium impregnated with stock solution of the synthesized complexes during incubation under certain conditions. Potential antibacterial activity can be further traced quantitatively. Usually, several methods are used together for the specific area of applications. Moreover, many methods can be compared one to other

Methods	**Characterization**	**Application**	**Explanation**
Uv visible	[60, 61]		Characterization of compounds structures.
		[68]	For the analysis of colored compound when probing SO_x and NH_3 reduction.
IR	[13, 15, 24, 66, 68, 73]		For the characterization of functional groups after reactions, characterization of chalcogen dopants on silicon. Sorption study of selenium(IV) solution on natural zeolites
		[15]	Investigation on fabrication of silicon based new material by near infrared analysis.
Luminescence	[27]		Characterization of chalcogen compounds by spectral luminescence study.
XRD	[13, 20, 21, 23, 24, 51–53, 60, 61, 73]		Determination of crystallinity of materials and its combination, for characterization of intermolecular interactions, the effect of chalcogen substitution
NMR	[2, 5, 13, 27, 28, 61–64]		Characterization of hydrogen and carbon- containing groups, also Se and Te NMR for chalcogen elements in the molecules
		[81–85]	For the mobility of small molecules in porous oxide materials, testing of chalcogen material application

Methods	Characterization	Application	Explanation
Mass spectrometer	[13]		Characterization of compounds synthesized
		[86]	For the determination of volatile compounds released from the silica oxides materials, testing of chalcogen materials application
Atomic spectroscopy	[10]		Quantitative measurement of selenium content in soil using HG atomic fluorescence spectroscopy
Optical microscopy	[18, 24, 85]		Surface texture characterization, as well as structural components of chalcogen materials.
Chromatography		[20, 86]	Separation of plant pigments on surface of silica materials, as one application for chalcogen compounds
Thermoanalysis	[3, 13, 64, 65, 80]		Characterization of chalcogen compounds, thermal clusters on chalcogen materials, formation of Zinc and cadmium sulfide and selenide, the study of degradation of palladium thiolate and selenolate
Magnetic analysis	[56, 60, 61, 75]		Characterization of magnetic nanoparticle of chalcogen materials, the effect of chalcogen substitution, suggestions for shape of complex metal chalcogenides together with electronic transition results.
Electrochemistry	[4]		Characterizing molecules based on reactions of chalcogen compounds
		[49, 69, 74]	Voltammetric measurement for application chalcogen doped Mo as electrode, photoelectrochemical solar cells with chalcogen materials
SEM	[18, 24, 48, 54, 60, 66–68]		Describing porous texture of the surface
EDX	[24, 64]		Describing the composition of elements of materials, characterization of Pd_4S and $Pd_{15}Se_{17}$
Bioassay		[60, 61]	Testing bioactivity of the chalcogen materials (thiourea).
Computation methods	[52, 53]		Calculation on S···O chalcogen bonds and modeling

Table 1. Chalcogen (including oxygen) materials analysis using available analytical techniques.

since some treatments are meant to be complementary to others. Method validation between more than one approach would be important. **Table 1** presents some available analytical methods for characterization and testing the applications.

In modern information technology, new challenges come from big data handling too. Most recent development in the handling of chemistry data, qualitative and quantitative can provide more information about the materials. Chemometrics has also become an important analytical chemistry tool in many disciplines including chemistry and other applied chemistry fields (e.g., biochemistry and bioinorganic chemistry). The data analysis gives trends, and this hypothetical analysis creates continuity in the investigation. Thus, the challenges of analytical chemistry are real, yet exalting!

7. More accounts on development of chemistry now and for the future

It is clear that there is an increasing demand for modern materials for various industry applications [67]. Therefore, modern analysis is needed to ensure that the synthesis of these newly made materials complies with quality attributes and satisfy their purposes. With the emergence of new devices, information technology and materials for big data handling, demand in the field of health and the pharmaceutical sector, as well as materials for application in science and the environment, are all factors bound to accelerate research to produce more types of new materials. At this point in time, chemistry is the key in technological and engineering developments, as everything can be manipulated from molecular [87] to structural levels. Chemistry education has the perspective of chemistry contextualization to socio-scientific orientation [88]. Awareness of chemistry concepts and also biochemistry is crucial in chemistry teaching, since the chemistry content alone is not enough to shape up the scientific attitude. When technology reigns, without good attitude of the chemist behind that, then the society as well as the future as a whole is in danger. So, it is clear here, that chemistry education is important for the right technology for the benefit of mankind.

Last but not the least, material science is a new fascinating area of interest attracting more and more scientists around the world. The need of raw materials leading to earth exploration and exploitation especially in mining has shifted the natural equilibrium to some extent and in turn will move as a self-reorganization phenomenon which in the context of human and other living being is categorized as a disaster. In this case, scientist must work within the scope of ethics since any changes from structural level, from chemistry level can develop up to environmental level. The idea of green chemistry has been developed due to new awareness of imbalancing nature by human activity. Chemistry education has to be more “eco-reflexive” [89] and technology must develop the environment with responsibility.

8. Conclusion

One of the main problems analytical chemist has to face is the lack of compositional and structural information concerning chalcogens and related chemical compounds and materials. The development of efficient procedures for the synthesis, extraction, and characterization or structural determination of this class of compounds is bottleneck of each analysis, for both characterization as well as optimization and applications. Thus, the analytical protocol for such analysis usually performed with the use of a wide range of techniques, both single and hyphenated, should be designed on the basis of the need to provide required knowledge about translocation of the metal and character of its interactions with examined chalcogen materials or compounds toward establishing goal oriented method. Method development as well as validation is, therefore, crucial in shaping future technology development and application of chalcogen and chalcogenides. Analytical chemistry premised on new ideas out of human creativity is set to shape future technology for chalcogen materials.

Conflict of interest

We declare that this chapter has no "conflict of interest."

Author details

Surjani Wonorahardjo*, Fariati Fariati and I Wayan Dasna

*Address all correspondence to: surjani.wonorahardjo@um.ac.id

Chemistry Department, Faculty of Mathematics and Science, State University of Malang, Malang, Indonesia

References

[1] El-Ramady HR, Domokos-Szabolcsy É, Abdalla NA, Alshaal TA, Shalaby TA, Sztrik A, et al. Selenium and nano-selenium in agroecosystems. Environmental Chemistry Letters. 2014;**12**(4):495-510

[2] El-Ramady H, Abdalla N, Taha HS, Alshaal T, El-Henawy A, Faizy SEDA, et al. Selenium and nano-selenium in plant nutrition. Environmental Chemistry Letters. 2016; **14**(1):123-147

[3] Devillanova F. Handbook of Chalcogen Chemistry [Internet]. Vol. 2. Cambridge: RSC Publishing, The Royal Society of Chemistry; 2013. P001-588p. Available from: http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Handbook+of+Chalcogen+Chemistry#1%5Cn. http://dx.doi.org/10.1039/9781849737463

[4] Glass RS. Redox chemistry of sulfur, selenium and tellurium compounds. In: Woollins JD, Selenium, Laitinen RS, editors. Tellurium Chemistry [Internet]. Berlin: Springer; 2011. pp. 57-77. Available from: http://link.springer.com/10.1007/978-3-642-20699-3

[5] Mugesh G, Panda A, Singh HB. Aspects of organochalcogen (S, Se, Te) compounds stabilized by intramolecular coordination. Journal of Chemical Sciences. 2000;**112**(3):239-248

[6] Harris JC, Cottrell SL, Plummer S, Lloyd D. Antimicrobial properties of *Allium sativum* (garlic). Applied Microbiology and Biotechnology. 2001;**57**(3):282-286

[7] Khalid N, Ahmed I, Latif MSZ, Rafique T, Fawad SA. Comparison of antimicrobial activity, phytochemical profile and minerals composition of garlic *Allium sativum* and *Allium tuberosum*. Journal of Korean Society for Applied Biological Chemistry. 2014;**57**(3):311-317

[8] Fordyce FM. Selenium deficiency and toxicity in the environment. In: Selinus O. editors. Essentials of Medical Geology. Revised ed. Dordrecht: Springer; 2013

[9] Fernández-Martínez A, Charlet L. Selenium environmental cycling and bioavailability: A structural chemist point of view. Reviews in Environmental Science and Biotechnology. 2009;**8**(1):81-110

[10] Wang J, Li H, Li Y, Yu J, Yang L, Feng F, et al. Speciation, distribution, and bioavailability of soil selenium in the Tibetan plateau Kashin-beck disease area—A case study in Songpan County, Sichuan Province, China. Biological Trace Element Research. 2013; **156**(1-3):367-375

[11] Van Geem M, Harvey JA, Cortesero AM, Raaijmakers CE, Gols R. Interactions between a belowground herbivore and primary and secondary root metabolites in wild cabbage. Journal of Chemical Ecology [Internet]. 2015;**41**(8):696-707. Available from: http://link.springer.com/10.1007/s10886-015-0605-7

[12] Frolov KA, Dotsenko VV, Krivokolysko SG, Kostyrko EO. Novel [4 + 2] cycloaddition reaction of aryl-methylidenemalononitriles to unsaturated chalcogen amides. Synthesis, structure, and properties of triethylammonium 3,5,5-tricyano-1,4,5,6- tetrahydropyridine-2-selenolates and -thiolates. Chemistry of Heterocyclic Compounds. 2013;**49**(9):1289-1300

[13] Ilyin IY, Pushkarevsky NA, Shapovalov SS, Pasynskii AA, Konchenko SN, Scheer M, et al. Chalcogen arsenide clusters of iron with a functional carboxyl group: Synthesis, structures, and thermolysis. Russian Journal of Coordination Chemistry [Internet]. 2012;**38**(10):662-670. Available from: http://link.springer.com/10.1134/S1070328412100065

[14] Shieh M. Recent developments of tellurium- and selenium-containing iron carbonyl clusters. Journal of Cluster Science [Internet]. 1999;**10**(1):3-36. Available from: http://www.scopus.com/inward/record.url?scp=0033481657&partnerID=8YFLogxK%5Cn http://www.scopus.com/inward/citedby.url?scp=0033481657&partnerID=8YFL ogxK

[15] Du L, Wu Z, Shi Y, Li S, Jiang Y. Comparison of near-infrared absorption and photoresponse of silicon doped with Se and Te via fs-laser irradiation. Applied Physics B [Internet]. 2017;**123**(12):283. Available from: http://link.springer.com/10.1007/s00340- 017-6861-1

[16] Gupta A, Kumar S, Singh HB. Structural and reactivity aspects of organoselenium and tellurium cations. Proceedings of the National Academy of Sciences, India, Section A: Physical Sciences. 2016;**86**(4):465-498

[17] Király B, Tárkányi F, Takács S, Kovács Z. Excitation functions of proton induced nuclear reactions on natural tellurium up to 18 MeV for validation of isotopic cross sections. Journal of Radioanalytical and Nuclear Chemistry. 2006;**270**(2):369-378

[18] Zonaro E, Piacenza E, Presentato A, Monti F, Dell'Anna R, Lampis S, et al. *Ochrobactrum* sp. MPV1 from a dump of roasted pyrites can be exploited as bacterial catalyst for the biogenesis of selenium and tellurium nanoparticles. Microbial Cell Factories [Internet]. 2017;**16**(1):1-17. Available from: https://doi.org/10.1186/s12934-017-0826-2

[19] Yang F, Chen L, Hu Q, Pan G. Effect of the application of selenium on selenium content of soybean and its products. Biological Trace Element Research. 2003;**93**(1-3):249-256

[20] Wonorahardjo S, Wijaya AR, Suharti S. Surface behavior of Rhodamin and Tartrazine on silica-cellulose sol-gel surfaces by thin layer elution. The Journal of Pure and Applied Chemistry Research. 2016;**5**(May):48-54

[21] Wonorahardjo S, Ibnu MS, Budiasih E. Original research paper sulfur dioxide and ammonia gas reduction using coconut cellulose and acetylated. Cellulose. 2016;**17**(2):179-188

[22] Dasna IW, Golhen S, Ouahab L, Peña O, Guillevic J, Fettouhi M. 1-D mixed stack of coordinated and uncoordinated radicals in Mn II (NITpPy) 4 [N (CN) 2] 2 (NITpPy = nitronyl nitroxide radical). Journal of the Chemical Society, Dalton Transactions [Internet]. 2000;**2**:129-132. Available from: http://pubs.rsc.org/en/content/articlelanding/2000/dt/a908891a/unauth#!divAbstract

[23] Dasna IW, Golhen S, Ouahab L, Fettouhi M, Pena O, Daro N, et al. Synthesis, X-ray crystal structures and magnetic properties of Cu (II)$(NITpPy)_2$ $[N(CN)_2]_2$ solv (NITpPy = nitronyl nitroxide radical, solv= H_2O or CH_3CN). From discrete molecules to 2-D polymeric coordination compounds. Inorganica Chimica Acta [Internet]. 2001;**326**(1):37-46. Available from: https://www.sciencedirect.com/science/article/pii/S0020169301005928

[24] Fariati F, Istikfaroh N, Effendy E, Ayu Darojah L. Synthesis and characterization of coordination compounds of silver(I) nitrite with ligands ethylenethiourea and N,N′-diethylthiourea. The Journal of Pure and Applied Chemistry Research [Internet]. 2016; **5**(3):142-147. Available from: http://jpacr.ub.ac.id/index.php/jpacr/article/view/253/pdf

[25] Dasna I, Golhen S, Ouahab L, Daro N, Sutter J-P. Ferromagnetic interactions in Mn(II) coordination complex containing nitronyl nitroxide radical and silver–dicyanide anion: Structure and magnetic studies of Mn II (NITpPy) 2 $[Ag (CN)_2]_2$. Polyhedron [Internet]. 2001;**20**(11):1371-1374. Available from: https://www.sciencedirect.com/science/article/pii/S0277538701006210

[26] Dasna I, Golhen S, Ouahab L, Daro N, Sutter J-P. Synthesis, X-ray crystal structures and magnetic properties of Cu II and Mn II complexes containing imino nitroxide radicals and a dicyanamide anion. New Journal of Chemistry [Internet]. 2001;**25**(12): 1572-1576. Available from: http://pubs.rsc.org/en/content/articlelanding/2001/nj/b104773f/unauth#!divAbstract

[27] Knyukshto VN, Volkovich DI, Gladkov LL, Kuzmitsky VA, Ul-Haque A, Popkova IA, et al. Phenyl substituted Mg porphyrazines: The effect of annulation of a chalcogen-containing heterocycle on the spectral-luminescent properties. Optics and Spectroscopy [Internet]. 2012;**113**(4):359-375. Available from: http://link.springer.com/10.1134/S0030400X12070119

[28] Naumov NG, Brylev KA, Mironov YV, Cordier S, Fedorov VE. Octahedral clusters with mixed inner ligand environment: Self-assembly, modification and isomerism. Journal of Structural Chemistry [Internet]. 2014;**55**(8):1371-1389. Available from: http://link.springer.com/10.1134/S0022476614080010

[29] Naumov NG, Virovets AV, Fedorov VE, Branch S. Octahedral rhenium(ILL) chalcocyanide cluster anions: Synthesis, structure, and solid state design. Journal of Structural Chemistry. 2000;**41**(3)

[30] Fajaroh F, Setyawan H, Sutrisno N, Wonorahardjo S. To enhance the purity and crystallinity of magnetite nanoparticles prepared by surfactant-free electrochemical method by imposing higher voltage. AIP Conference Proceedings. 2014;**1586**:179-182

[31] Jang HJ, Lee HJ, Yoon DK, Ji DS, Kim JH, Lee CH. Antioxidant and antimicrobial activities of fresh garlic and aged garlic by-products extracted with different solvents. Food Science and Biotechnology [Internet]. 2018;**27**(1):219-225. Available from: https://doi.org/10.1007/s10068-017-0246-4

[32] Sun YE, Wang W. Changes in nutritional and bio-functional compounds and antioxidant capacity during black garlic processing. Journal of Food Science and Technology. 2018;**55**(2):479-488

[33] Beato VM, Orgaz F, Mansilla F, Montaño A. Changes in phenolic compounds in garlic (*Allium sativum* L.) owing to the cultivar and location of growth. Plant Foods for Human Nutrition. 2011;**66**(3):218-223

[34] Afzal M, Ali M, Thomson M, Armstrong D. Garlic and its medicinal potential. Inflammopharmacology. 2000;**8**(2):123-148

[35] Nam H, Jung H, Kim Y, Kim B, Kim KH, Park SJ, et al. Aged black garlic extract regulates lipid metabolism by inhibiting lipogenesis and promoting lipolysis in mature 3T3-L1 adipocytes. Food Science and Biotechnology [Internet]. 2017;**27**:3-7. Available from: http://link.springer.com/10.1007/s10068-017-0268-y

[36] Sato E, Kohno M, Hamano H, Niwano Y. Increased anti-oxidative potency of garlic by spontaneous short-term fermentation. Plant Foods for Human Nutrition. 2006; **61**(4):157-160

[37] Lanzotti V. Bioactive polar natural compounds from garlic and onions. Phytochemistry Reviews. 2012;**11**(2-3):179-196

[38] Da ZZ, Liang YZ, Xu CJ. Comparing chemical fingerprints of herbal medicines using modified window target-testing factor analysis. Analytical and Bioanalytical Chemistry. 2005;**381**(4):913-924

[39] Park EJ, Pezzuto JM. Botanicals in cancer chemoprevention. Cancer Metastasis Reviews. 2002;**21**(3-4):231-255

[40] Zhu Q, Kakino K, Nogami C, Ohnuki K, Shimizu K. An LC-MS/MS-SRM method for simultaneous quantification of four representative organosulfur compounds in garlic products. Food Analytical Methods [Internet]. 2016;**9**(12):3378-3384. Available from: http://dx.doi.org/10.1007/s12161-016-0535-1

[41] Zalepugin DY, Tilkunova NA, Chernyshova IV. Stability of thiosulfinates from garlic (*Allium sativum* L.) supercritical extracts in polar and nonpolar solvents. Russian Journal of Physical Chemistry B [Internet]. 2015;**9**(7):1032-1042. Available from: http://link.springer.com/10.1134/S1990793115070143

[42] Zalepugin DY, Til'kunova NA, Chernyshova IV, Mulyukin AL. Sulfur-containing components of supercritical garlic extracts and their synthetic analogs as potential biocides. Russian Journal of Physical Chemistry B [Internet]. 2013;**7**(7):843-848. Available from: http://link.springer.com/10.1134/S1990793113070154

[43] Yenigün B, Güvenilir Y. Partial purification and kinetic characterization of acid phosphatase from garlic seedling. Applied Biochemistry and Biotechnology: Part A: Enzyme Engineering and Biotechnology [Internet]. 2003;**107**(1-3):677-688. Available from: https://www.scopus.com/inward/record.uri?eid=2-s2.0-0038748235&doi=10.1385%2FABAB%3A107%3A1-3%3A677&partnerID=40&md5=8c453555f4a1d895ce46d7fa12de161e

[44] Harborne JB. Phytochemical methods; a guide to modern techniques of plant analysis. Journal of Chemical Information and Modeling. 1998;**3**:317

[45] Endo A, Imai Y, Nakamura M, Yanagisawa E, Taguchi T, Torii K, et al. Distinct intraspecific variations of garlic (*Allium sativum* L.) revealed by the exon-intron sequences of the alliinase gene. Journal of Natural Medicines. 2014;**68**(2):442-447

[46] Khaghani S, Ghanbari D. Magnetic and photo-catalyst Fe_3O_4–Ag nanocomposite: Green preparation of silver and magnetite nanoparticles by garlic extract. Journal of Materials Science: Materials in Electronics. 2017;**28**(3):2877-2886

[47] Saman N, Johari K, Mat H. Synthesis and characterization of sulfur-functionalized silica materials towards developing adsorbents for mercury removal from aqueous solutions. Microporous and Mesoporous Materials [Internet]. 2014;**194**:38-45. Available from: http://dx.doi.org/10.1016/j.micromeso.2014.03.036

[48] Tull BR, Winkler MT, Mazur E. The role of diffusion in broadband infrared absorption in chalcogen-doped silicon. Applied Physics A: Materials Science & Processing. 2009;**96**(2):327-334

[49] Romanov RI, Fominski VY, Shelyakov AV, Golubkov GV. Structure and catalytic properties of MoSex thin films containing Mo nanoparticles in electrochemical production of hydrogen in solution. Russian Journal of Physical Chemistry B [Internet]. 2016;**10**(2):238-244. Available from: http://link.springer.com/10.1134/S1990793116020238

[50] Sharma A, Mehta N. Optical characterization of tin containing novel chalcogen rich glassy semiconductors. Optical and Quantum Electronics [Internet]. 2018;**50**(2):1-13. Available from: https://doi.org/10.1007/s11082-018-1386-3

[51] Mahmudov KT, Kopylovich MN, Guedes da Silva MFC, Pombeiro AJL. Chalcogen bonding in synthesis, catalysis and design of materials. Dalton Transactions [Internet]. 2017;**46**(31):10121-10138. Available from: http://xlink.rsc.org/?DOI=C7DT01685A

[52] Shishkin OV, Omelchenko IV, Kalyuzhny AL, Paponov BV. Intramolecular S···O chalcogen bond in thioindirubin. Structural Chemistry. 2010;**21**(5):1005-1011

[53] Pascoe DJ, Ling KB, Cockroft SL. The origin of chalcogen-bonding interactions. Journal of the American Chemical Society. 2017;**139**(42):15160-15167. DOI: 10.1021/jacs.7b08511

[54] Pleshchev VG, Baranov NV, Mart'yanova IA. Structural phase transformations and physical properties of intercalation compounds in the $Cr_{0.5}Ti(Se_{1-x}Te_x)_2$ system. Physics of the Solid State [Internet]. 2006;**48**(10):1959-1964. Available from: http://link.springer.com/10.1134/S1063783406100246

[55] Baranov NV, Pleshchev VG, Sherokalova EM, Selezneva NV, Volegov AS. Influence of the chalcogen substitution on the character of magnetic ordering in $Fe_{0.5}TiS_{2-x}Se_x$ intercalated compounds. Physics of the Solid State [Internet]. 2011;**53**(4):701-706. Available from: http://link.springer.com/10.1134/S1063783411040044

[56] Posth O et. al. Classification of analysis methods for characterization of magnetic nanoparticle properties. In: Proceeding of XXI IMEKO World Congress, Measurement in Research and Industry. Prague, Czech Republic. August 30 September 4, 2015

[57] Badaloni M, Rossi M, Chiappini G, Lava P, Debruyne D. Impact of experimental uncertainties on the identification of mechanical material properties using DIC. Experimental Mechanics. 2015;**55**(8):1411-1426

[58] Bordovsky GA, Gladkikh PV, Kozhokar MY, Marchenko AV, Seregin PP, Terukov EI. Tin impurity centers in glassy germanium chalcogenides. Semiconductors [Internet]. 2011;**45**(10):1346-1351. Available from: http://link.springer.com/10.1134/S1063782611100058

[59] Bordovsky GA, Nemov SA, Marchenko AV, Seregin PP. Mössbauer studies of two- electron centers with negative correlation energy in crystalline and amorphous semiconductors. Semiconductors [Internet]. 2012;**46**(1):1-21. Available from: http://link.springer.com/10.1134/S1063782612010071

[60] Ajibade PA, Zulu NH, Oyedeji AO. Synthesis, characterization, and antibacterial studies of some metal complexes of dialkyl thiourea: The X-ray single crystal structure of $[CoCl_2(detu)_2]$. Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry [Internet]. 2013;**43**(5):524-531. Available from: http://www.tandfonline.com/doi/abs/10.1080/15533174.2012.741179

[61] Ajibade PA, Zulu NH. Synthesis, characterization, and antibacterial activity of metal complexes of phenylthiourea: The X-ray single crystal structure of $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2]\,C_2HOH$. Journal of Coordination Chemistry. 2010;**63**(18):3229-3239

[62] Preetha KC, Remadevi TL. Band gap engineering in PbSe thin films from near-infrared to visible region by photochemical deposition method. Journal of Materials Science: Materials in Electronics. 2014;**25**(4):1783-1791

[63] Nucci A, Marino-Merlo F, De Nisco M, Pedatella S, Rossi F, Jacob C, et al. Se-(2-aminoalkyl)selenocysteines as biochemical redox agents. A tool to contrast cell injury induced by aflatoxin B1 in HepG2 cells. Amino Acids. 2014;**46**(2):459-470

[64] Jain VK. Synthesis and characterization of single-source molecular precursors for the preparation of metal chalcogenides. Journal of Chemical Sciences. 2006;**118**(6):547-552

[65] Malik MR, Vasylyeva V, Merz K, Metzler-Nolte N, Saleem M, Ali S, et al. Synthesis, crystal structures, antimicrobial properties and enzyme inhibition studies of zinc(II) complexes of thiones. Inorganica Chimica Acta [Internet]. 2011;**376**(1):207-211. Available from: http://dx.doi.org/10.1016/j.ica.2011.06.017

[66] Del CR, Criado JJ, Gheorghe R, González FJ, Hermosa MR, Sanz F, et al. N- benzoyl-N′-alkylthioureas and their complexes with Ni(II), Co(III) and Pt(II)—Crystal structure of 3-benzoyl-1-butyl-1-methyl-thiourea: Activity against fungi and yeast. Journal of Inorganic Biochemistry. 2004;**98**(8):1307-1314

[67] Rooney M, Roberts JC, Murray GM, Romenesko BM. Advanced materials: Challenges and opportunities. 2000;**21**(4):516-527

[68] Wonorahardjo S, Ibnu MS, Budiasih E. Sulfur dioxide and ammonia gas reduction using coconut cellulose and acetylated cellulose. Scientific Study and Research: Chemistry and Chemical Engineering, Biotechnology, Food Industry. 2016;**17**(2):179-188

[69] Kozytskiy AV, Stroyuk OL, Raevskaya AE, Kuchmy SY. Photoelectrochemical solar cells with semiconductor nanoparticles and liquid electrolytes: A review. Theoretical and Experimental Chemistry. 2017;**53**(3):145-179

[70] Dutt MB, Sharma BL. 3 Diffusion in compound semiconductors. Diffusion in Semiconductors SE- 10 [Internet]. 1998;**33A**:1-63. Available from: http://dx.doi.org/10.1007/10426818_10

[71] Stuart BH. Infrared spectroscopy: Fundamentals and applications [Internet]. Methods. 2004;**8**:224. Available from: http://doi.wiley.com/10.1002/0470011149

[72] Frumar M et al. Crystalline and amorphous chalcogenides, high-tech materials with structural disorder and many important applications. In: Bardosova M, Wagner T, editors. Nanomaterials and Nanoarchitectures: A Complex Review of Current Hot Topics and their Applications. Netherlands: Springer; 2015

[73] Zonkhoeva EL, Sanzhanova SS. Infrared spectroscopy study of the sorption of selenium(IV) on natural zeolites. Russian Journal of Physical Chemistry A [Internet]. 2011;**85**(7):1233-1236. Available from: http://link.springer.com/10.1134/S0036024411070399

[74] Bouroushian M. In: Scholz F, editor. Electrochemistry of Metal Chalcogenides. Heidelberg: Springer Berlin Heidelberg; 2010

[75] Baranov NV, Gerasimov EG, Mushnikov NV. Magnetism of compounds with a layered crystal structure. Physics of Metals and Metallography [Internet]. 2011;**112**(7):711-744. Available from: http://dx.doi.org/10.1134/S0031918X11070039

[76] Nilges T, Bawohl M, Lange S, Messel J, Osters O. Highly dynamic chalcogen chains in silver(I) (Poly)chalcogenide halides: A new concept for thermoelectrics? Journal of Electronic Materials. 2010;**39**(9):2096-2104

[77] Kehr M, Fatkullin N, Kimmich R. Molecular diffusion on a time scale between nano- and milliseconds probed by field-cycling NMR relaxometry of intermolecular dipolar interactions: Application to polymer melts. The Journal of Chemical Physics. 2007;**126**(9):094903-094903-8

[78] Fatkullin N, Kimmich R. Theory of field-gradient NMR diffusometry of polymer segment displacements in the tube-reptation model. Physical Review E [Internet]. 1995; **52**(3):3273-3276. Available from: http://link.aps.org/doi/10.1103/PhysRevE.52.3273

[79] Leszczynski J, (series editor). Challenges and advances in computational chemistry and physics. In: Scheiner S, editor. Noncovalent Forces. Cham: Springer; 2006 [Internet]. 1-680 p. Available from: http://link.springer.com/content/pdf/10.1007/1-4020-4850-5.pdf%5Cnpapers2://publication/uuid/F8F76DC1-C945-42AF-AD3E-05DEC2D420DE

[80] Saito M, Kikuchi K. Infrared optical fiber sensors. Optical Review. 1997;**4**(5):527-538

[81] Mattea C, Kimmich R, Ardelean I, Wonorahardjo S, Farrher G. Molecular exchange dynamics in partially filled microscale and nanoscale pores of silica glasses studied by field-cycling nuclear magnetic resonance relaxometry. The Journal of Chemical Physics. 2004;**121**(21):10648-10656

[82] Ardelean I, Mattea C, Farrher G, Wonorahardjo S, Kimmich R. Nuclear magnetic resonance study of the vapor phase contribution to diffusion in nanoporous glasses partially filled with water and cyclohexane. The Journal of Chemical Physics [Internet]. 2003;**119**(19):10358. Available from: http://link.aip.org/link/JCPSA6/v119/i19/p10358/s1&Agg=doi

[83] Kimmich R. NMR-Tomography, Diffusometry, Relaxometry. Berlin: Springer Berlin Heidelberg; 1997. 526p

[84] Wonorahardjo S, Ball G, Hook J. Moran G. NMR relaxation studies of porous sol-gel glasses. Magnetic Resonance Imaging [Internet]. 1998;**16**(5-6):511-513. Available from: http://www.ncbi.nlm.nih.gov/pubmed/9803899

[85] Wonorahardjo S, Ball GE, Hook J, Moran G. 2H NMR relaxation monitoring of gelation in tetramethoxysilane sol-gels. Journal of Non-Crystalline Solids [Internet]. 2000;**271**(1–2):137-146. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0022309300000685

[86] Nurindah N, Wonorahardjo S, Adi Sunarto D, Sujak S. Chemical cues in tritrophic interaction on biocontrol of insect pest. The Journal of Pure and Applied Chemistry Research [Internet]. 2017;**6**(1):49-56. Available from: http://jpacr.ub.ac.id/index.php/jpacr/article/view/282/pdf

[87] Sjöström J. The discourse of chemistry (and beyond). HYLE International Journal for Phylosophy of Chemistry. 2007;**13**(2):83-97

[88] Sjöström J, Talanquer V. Humanizing chemistry education: From simple contextualization to multifaceted problematization. Journal of Chemical Education. 2014;**91**(8):1125-1131

[89] Sjöström J, Eilks I, Zuin VG. Towards eco-reflexive science education. Science & Education [Internet]. 2016;**25**(3-4):321-341. Available from: http://link.springer.com/10.1007/s11191-016-9818-6