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PREFACE

Chemistry – Human Heritage

Palaeolithic period of the Stone Age represents the longest and most mysterious period in the development of human history and chemistry as well. In accordance with the orthodox view on the history of chemistry its knowledge originates a legend, in which embodied poeticised reality carries historical truth.

150 000 years B.C. in Palaeolithic period a human with the ability to observe and experiment made use of gaining fire accidentally and subdued the nature. Fire as a first "invention" served production of all other tools. Burning enabled further use of disclosed basic chemical changes of the substance. The fire chemistry developed through the ability of controlled handling of flame in pottery making, metallurgy as well as glass-making industry. Well-preserved paintings of cave art from the period around 30 000 years B.C. show traces of "animism", religion of Stone Age people ruled by ghosts. Colour pigment was fired ore compounding of the manganese or iron oxides-hydroxides. Towards the end of the Ice Age Front Asia and Central Europe were affected by fatal floods (The deluge), which caused the doom of fossil people and their admirable culture.

In Mesopotamia there were preserved only fragments of their cultural heritage such as fragments of earthen buildings, ceramic vessels and other objects from the period of 14 000 years B.C. All events were carried over in oral tradition. Therefore the only evidence to prove the fact of floods (The deluge) is included in the Sumerian record from the 20th and 18th centuries B.C. taken over by the Babylonians, Assyrians and Jews. It became also a part of other ancient mythologies.

Around 8700 B.C. the Sumerians resettled the area of Mesopotamia. Their culture is known for building tower-like brick temples and terraces of imposing architecture. The achievements and technical conveniences used in metallurgy helped to solve the problem of complex chemical reaction of smelting of metals and their enrichment. 4000 years B.C. people used drifted earth in miscellaneous ways, e.g. decorating the front of brick buildings with ceramic glazed mosaic. At that time glass making was invented. Oilfields in the Euphrates basin were used as fuel. Around 3800 B.C. the Front East became a place of boom of Sumerian civilization from the chemical practice point of view.

About 700 years later developed Sumerian civilisation gave birth to the Egyptian one, which derived from the Sumerians the knowledge of chemistry, writing and many other skills. The Egyptians disclosed complex chemical reactions through trial and error. They managed to prepare soda, potash, various inorganic and organic colorants and pigments, alum and green vitriol. They were able to tan animal skin using salt, lime and various plant extracts. Egyptian chemists were highly qualified and skilled technicians closely related to the church and court. At the same time they were black handcraft workers with huge magic abilities. Generally speaking there is no evidence on the theory of chemistry available from the early stages of the Bronze Age (2700-700 B.C.), though there are signs of general basic procedures to be traced.

There are alchemic ideas to be found in old religious literature and opinions on metal "growths" and transformation in Burma, China, India, and in some African parts before 1500 B.C. Above all the Chinese alchemy was closely connected with empiric experiments and featured chemistry as a subject based on observing facts and thoroughly carried out experiments. At the beginning of the 11th century B.C. their knowledge was derived from the work of Wu-sing. Chinese alchemy was mainly affected by the ideas of tacisms around the 6th century B.C.

The birth of chemistry as a scientific field dates back to 900–600 years B.C. The Grecian culture flourished between the 5th and 4th centuries B.C. among others thanks to the cultural heritage of the Front East unlike the idea of the Egyptians being considered their spiritual fathers. The main chain links were Syria and Anatolia, which served as an access to the knowledge of older civilisations.

Atomistic hypothesis of Grecian philosophic conception built an important milestone for any further chemical development in The Middle Ages. The most significant representative of antique atomistic views was Democritus strongly opposed by Platon. The most outstanding of Platon's pupils was Aristotle (384–322 B.C.) – the most versatile antique philosopher. His ideas about structure of substances and conversion of the elements were universally accepted and played an important role in alchemy, when it was scientifically recognized and supported by Mendeleyev's Periodic Law in 1869.

We have no time information available concerning the birth of alchemy in old Egypt. Hellenic period (336 B.C.–30 A.D.) was considered the beginning of alchemy from the western point of view and its classical image consisting of practical, occult and philosophical sciences. In the beginning there was only literature in Greek available put together by father of alchemy Hermes Trismegistos in Alexandria. His tractate „Emerald board" represents a kind of alchemic code comprising of basic ideas expressed in very poetic language and cryptograms. The Egyptian priests practised two kinds of alchemy – practical (exoteric) and mystic (esoteric).

In the 7th century the world of science and art had to face the tragedy of the famous library in Alexandria being destroyed by fire. Luckily the school itself was saved and changed into Arabian one. Under the reign of liberal caliphs the whole range of academies and scientific schools arose and their main task was to spread knowledge around the whole world. The most famous author of that time was Abú Abdallah Džabir Ibn Hajjan. The Christians called him Geber and he was considered the inventor and author of many works on chemistry of that time. His chemical reactions were paraphrased and the processes were anthropomorphized. Avicena's (930–1037) philosophy was of Aristotle character containing mystic elements. Avicena transferred the knowledge of Grecian science and philosophy into the Arabic world. The Arabians revaluated old theories thanks to the results of their wide experimental experience and contributed significantly to the chemistry, and deserve to be called the founders of chemistry. They bequeathed enormously wide chemical knowledge in their experiments such as filtration, sublimation, distillation, various types of annealing and discovering many chemical compounds. Arabian science mediated the medieval Christian scientists the ancient knowledge and played an important role in the process of formation of theories of Paracelsus.

The future of chemistry was dependent on the first local chemical industry of Islamic countries, which produced in the large scale various goods such as essential oils, soda, alum, green vitriol, nitre and other salts, which were exported and used worldwide, particularly in textile industry.

In the early Modern Times new methods began to establish under the pressure of new knowledge, religious conflicts, exchange of ideas and information. At the beginning of Renaissance the general theory of chemistry began to form. Renaissance technology achieved the highest level of development in mining, metallurgy and alchemy. Georgius Agricola (1494–1555), a physician, who excelled in metallurgy, studied minerals and chemical reactions in ore processing in Jáchymov and recorded his findings in „De Re Metallica“.

Far more significant element was alum, which was used for many centuries in textile and leather industry and paper production. The first chemical trust,Societas Aluminium”, was founded by the Pope in 1462, however papal alum was expensive and the pursuit of its mining monopole failed. Production of alum in the Czech republic was first recorded in the 16th century.

The main representative of the top period of alchemy became Philipus Aureolus Theophrastus Bombastus Paracelsus von Hohenheim, born in 1493 in Eisiedeln near Zürich and died in Salzburg in 1541.

His approach to chemistry was animistic, intuitive. Until the 18th century he had the greatest influence on scientific development of chemistry and biochemistry. He drew his knowledge on the old Arabian alchemic traditions and was able to modify them. Paracelsus was the first to recommend chemistry to become a part of medical students´ lessons and required chemical laboratories to be founded at the faculties of medicine. In his „Buch Paragranum“(1531) Paracelsus started the real reform of alchemy. In 1537 he spent six months at the castle in Moravský Krumlov where he finished few of his most important works.

The interest in alchemy and alchemic knowledge was already spreading in Central and Western Europe from the beginning of the 11th century and towards the 13th century it became a renowned field of study booming under Emperor Rudolf II. (1552–1612). Under his reign Prague turned into the centre of alchemic laboratories and first teamwork led by Tadeáš Hájek from Hájek (1525–1612).

Towards the end of the 17th century alchemy strived for detailed elaboration of laboratory methods and preparation of chemical elements and new compounds.

In 1919, Ernst Rutherford was the first to fulfil the age-old alchemists’ desire by artificial transformation of atom.

Chemical system created by Lavoisier (1743–1794) and his colleagues divided all substances into simple (elements) and compact (compounds). This chemical system contributed to the progress of chemistry by defining and implementing rules in chemical terminology. New terminology caused as well a modification of old chemical symbols, which were no longer sufficient for the purposes of new oxidation theory and quick development of quantitative chemistry. The most important contribution of Lavoisier reaction in chemistry was enabling intellectual and quantitative comprehension of chemical processes.

During 1746–1751 there was the first „Society of unknowns – Societas incognitorum“ established by J. Petrasch and his friends in Olomouc. Its aim was to help new scientific ideas and inventions to spread throughout the Austro-Hungarian Monarchy.

Marie Therese in 1755 did away with alchemy and chemistry became an actual field of scientific studies.

In 1770 I.Born established a private society for mathematics, history and science in Prague. Later on it transformed into a public institution „Royal Academic Society of Science“, as a beginning of the Academy of Science.

Scientific revolutions are not accomplished at an empiric level of science but at a theoretical one, when the right theoretical conclusions are achieved through the process of generalizing new empiric facts.

Adolf G. Pokorný

1. PLENARY LECTURES

L01 ESSENTIALITY, SUPPLY AND TOXICITY OF TRACE AND ULTRATRACE ELEMENTS IN HUMAN NUTRITION – PROBLEMS AND RISKS

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In spite of international trade, the trace and ultratrace element offer to humans is varied by the geological origin and the environmental pollution of the soil on which food is produced, by the drinking water, the form of farming (conventional or ecological), and the mineral mixtures given to farm animals. Moreover, the trace und ultratrace element offer is significantly influenced by the changes that foodstuffs and beverages undergo during industrial processing (grinding, refining, filtering of beverages etc.).

The essentiality and toxicity of 21 trace and ultratrace elements were examined by the duplicate portion technique in 21 test populations in Germany and Mexico and the results compared with those of the basket method. The influence of gender, habitat, kind of diet, age, body weight, performance, time and season were examined with regard to the normative requirement and the tolerable daily intake of the trace elements Fe, Zn, Mn, Cu, Mo, Ni, I and Se and the ultratrace elements from Al up to U.

The normative human requirement of Mn, Mo and Ni was found to be satisfied. In man, deficiencies in Mn, Ni and Mo (with the exception of inborn Mo cofactor defects) were not registered. Mn deficiency is common in farm animals and game, whereas Mo and Ni deficiencies in animals were not observed. The iron and zinc intake of man has decreased during the last decennium, while that of copper has increased. A deficiency of Fe and Zn is possible in humans and animals everywhere in the world. I and Se deficiency is common in Europe but can be overcome by supplementation. The normative iodine requirement of humans and animals in Europe is met where salt iodinated with 20 mg I/kg and mineral feed mixes iodinated with 10 mg I/kg are used. A normalisation of the iodine metabolism is bound to a satisfied Se status. Se is necessary for the conversion of thyroxine to triiodine thyronine.

Table I
Daily intakes of trace and ultratrace elements by German adults with mixed diet, normative requirements, recommendations and tolerable daily intakes

Element	Intake		Normative requirement				Recommendation	Tolerable intake	
	Women	Men	Women	Men	kg body weight	Food dry matter		Day	μg/kg body weight
Fe μg/d	6300	7700	7000	6000	100	22 500	10 000	45 000	650
Zn μg/d	6000	7500	6000	8000	100	20 000	10 000	40 000	600
Mn μg/d	2400	2700	< 1000	< 1000	15	3500	2000	11 000	150
Cu μg/d	1100	1.200	700	800	11	2600	1200	10 000	140
I μg/d	83	113	65	75	1.0	250	200	500	7
Ni μg/d	90	97	25	35	0.4	100	50	1000	15
Mo μg/d	89	100	20	25	0.3	80	50	2000	30
Se μg/d	30	41	20	25	0.3	80	50	700	10
Al μg/d	3100	3200	< 2000	< 30	< 700	–	70 000	1000	
Sr μg/d	1800	2200	unknown	–	–	–	50 000	700	
Rb μg/d	1600	1700	< 100	< 1.5	< 350	–	20 000	300	
Li μg/d	713	990	< 100	< 1.5	< 350	–	10 000	150	
Ba μg/d	490	570	unknown	–	–	–	10 000	150	
Ti μg/d	80	90	< 50	< 0.70	< 150	–	–	–	
As μg/d	107	145	< 20	< 0.30	< 70	–	700	10	
Cr μg/d	61	84	< 20	< 0.30	< 70	50	5000	70	
V μg/d	11	33	< 10	< 0.15	< 30	–	1800	25	
Pb μg/d	19	19	< 10	< 0.15	< 35	–	250	3.5	
Cd μg/d	7.1	8.8	< 5	< 0.08	< 18	–	70	1.0	
Hg μg/d	2.7	4.8	unknown	–	–	–	50	0.7	
U μg/d	2.6	2.8	unknown	–	–	–	35	0.5	

Ultratrace elements are well known as toxic elements. Meanwhile their essentiality or beneficial role has been discovered by means of synthetic rations and very low concentrations of these elements. Their function as components of essential proteins, enzymes etc. has not yet been identified. After such identification, the respective element becomes a trace element. This happened after nickel and cobalt were discovered to be essential components of urease and vitamin B_{12}, respectively. The feed and foodstuffs taken by the test populations were found to meet the normative requirements of ultratrace elements. Deficiency symptoms were only to be expected in parenteral nutrition, and in genetic disorders which lower the absorption or the formation and effectiveness of the essential components (for example molybdopterin).

Al deficiency is known to impair reproduction performance. Rb is necessary for normal intrauterine development and pregnancy time, and Li for postnatal development and wellness, whereas Ti lowers the postnatal mortality. As influences the activity of the cardiac muscle. Cr is involved in the maintenance of the glucose tolerance, Pb influences haemoglobin synthesis, and Cd is required for muscle function. Other elements known to be needed for essential functions in animal and man are Br, F, V, B and Si.

Table I lists the human requirements of trace and ultratrace elements, recommended intakes, and, last but not least, the upper limits of tolerable intake per day and per kg body weight of adults. The risk of intoxication by excessive levels of trace and ultratrace elements through supplementation or anthropogenic pollution is highest for Fe (haemochromatosis, hypochromic anaemia), Cu (Indian childhood disease), I (hyperthyroidism), Ni (nickel allergy), Al (interactions with Ca, Mg, Zn), Li (side effects of Li therapy), As (cancer?), Cr (chromium allergy) and Hg (amalgams, Minamata disease). The risks of anthropogenic cadmium intoxication (Itai-Itai disease) and Pb contamination have decreased during the last decade.

Chronical intoxications with metals are frequently induced by interactions of the elements with “essential” elements (Pb → Fe; Ca, Mg; Mo → Cu; Cd → Cu, Zn, Fe; Ni → Zn, Mg, Mn; Al → Mg, Ca, Fe, Zn). These interactions induce secondary trace element deficiencies.

Generally, during the passage of inorganic components of foodstuffs, water and air through the fauna and man, which has been going on for several hundred millions of years, the majority of these components have most likely become parts or activators of proteins, enzymes or other essential compounds of the body. Consequently, both a deficiency and a toxic excess must be considered for most elements.

L02 ARE THE FOODS OF NATURAL ORIGIN ALWAYS HEALTHY?

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Introduction

Changing lifestyles in the developed countries is reflected by a pronounced public concern about environmental and personal health issues. Not surprisingly the demand for “healthy” and “natural” foods which are minimally processed and contain no artificial colours, flavourings, preservatives or sweeteners is rapidly growing. as well as the sale of food containing only ingredients from organic farming systems i. e. grown with “earth friendly” methods However, in addition to components responsible for wholesomeness – health beneficial/protective effects, foods may under certain circumstances contain various natural toxic components, some them are classified by toxicologists as a serious food safety issue and are or are considered to be regulated. In other words the popular notion equating “natural” and “healthy” is obviously not realistic since some natural food components may pose a far greater health risk as compared to residues of man-made chemicals represented by environmental pollutants[1]. As regards the later argument, a series breaking papers concerned with this issue were published by B. Ames[2] in early 90th who pointed out the misconception that human exposures to carcinogens and other toxins are nearly all due to synthetic chemicals (for details see below).

Definition of natural toxins

Several approaches are currently used to specify the term “natural toxins”:

The narrow definition specifies natural toxins as food constituents endogenously produced by food organisms and capable to give rise to adverse effects when the food organism or product thereof is consumed.

The broader definition of natural toxins includes also toxic compounds originating from a contamination of the food.

In addition to natural toxins and exogenous contaminants, human diet may contain various hazardous chemicals originated from natural precursors during (often thermal) processing. Acrylamide and 3-MCPD (3- monochloropropane-1,2-diol) are example of processing contaminants of the most recent concern.

Plant toxins

It should be noted that only a small number of existing plants is used for human nutrition or as food ingredients since many wild species contain sometimes even high concentrations of various antinutrients (compounds decreasing availability of nutrients) and/or compounds exhibiting toxic effects in humans and/or farm animals[3–5]. Alike other bioactive secondary plant metabolites, natural toxins are produced from intermediates and products of primary metabolism, the mutual relationships of main constituents is outlined in Fig. 1.

The reason for the presence of natural toxins in plants has not been fully elucidated yet. Nevertheless, they are assumed – at least under certain circumstances – to play a role of „naturally occurring pesticides" warding off the attack insects or other predators. Alternatively, toxic constituents may be formed to protect the plant from spoilage when damaged by weather, handling, UV light or microorganisms.

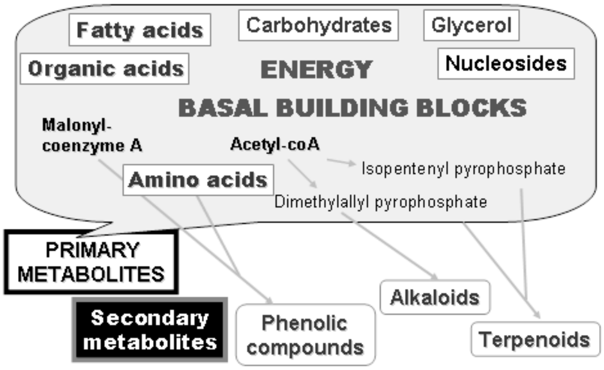

Fig. 1. **Formation of secondary metabolites in plants**

Domestification process over the years as well as ensuing selective breeding programs resulted in a gradual reducing the levels of natural toxins in cultural species. On the other hand decrease or even complete elimination of these "protective" constituents has unavoidably resulted in lowered resistance of modern cultivated plants to diseases and, consequently, to increased demands for use of synthetic pesticides to protect the crop against various pests.

Plant toxins can be separated into several groups; the most common criterion for classification is their chemical structure. In Table I, the most common classes of natural toxins as occurring in food crops identified within EU-Flair NETTOX project[6] are shown.

Table I
Main groups of food plant toxins

Toxicants	Plant family
Alkenyl benzenes	*Myristicaceae, Labiatae, Lauraceae, Piperaceae*
Anthraquinones	*Polygonaceae*
Capsaicinoids	*Solanaceae*
Coumarins	*Leguminosae, Rubiaceae, Umbelliferae*
Coumestans	*Leguminosae*
Cucurbitacins	*Cucurbitaceae*
Cyanogennic glycosides	*Leguminosae, Gramineneae, Rosaceae*
Furocoumarins	*Umbelliferae, Rutaceae*
Glukosinolates	*Cruciferae*
Glykoalkaloids	*Solanaceae*
Glycyrrhizinic acid	*Leguminosae, Sapindaceae*
Hydrazons	*Morchellaceae*
Proteinase inhibitors	*Leguminosae*
Isoflavonoids	*Leguminosae, Rosaceae, Vitaceae*
Lectins	*Leguminosae*
Nitriles	*Leguminosae*
Oligosaccharides	*Leguminosae*
Oxalates	*Chenopodiceae*
Phenylhydrazines	*Agaricaceae*
Pyrrolizidin alkaloids	*Asteracea, Boraginaceae, Leguminosae, Sapindaceae*
Quinolizidine alkaloids	Berberidaceae, Chenopodiaceae, *Leguminosae, Solanaceae*
Saponins	*Leguminosae*
Sesquiterpen lactones	*Asteraceae, Convolvulaceae, Rutaceae, Umbelliferae*
Toxic amino acids	*Leguminosae*
Toxic fatty acid	*Cruciferae*
Toxic pyrimidines	*Leguminosae*
Xanthin alkaloids	*Buttneriaceae, Rubiaceae, Theacea*

Microbial toxins

Considering the broader definition, toxic co-metabolites of microorganisms that may contaminate food (or raw material used for its production) can be also classified as natural toxins. Mycotoxins such as aflatoxins, ochratoxin A, trichothecenes, zearalenone, fumonisins and patulin produced by toxinogennic species of *Aspergillus, Penicillium, Fusarium* and other genera of fungi are of greatest concern both in terms of toxicity and worldwide occurrence in natural environment. Once contaminating food crops and/or animal products, their removal by common food processing practices is almost impossible (thermo labile patulin is an exception).

Also some bacteria may produce toxins. (e. g. botulin, *Staphylococcus aureus* enterotoxin and *Bacillus cereus* enterotoxin). Many of them are proteins which are not, contrary to most of mycotoxins, heat-stable and can be therefore in most cases reduced/eliminated by thermal treatment of contaminated matrix.

Phycotoxins

Some unicellular micro algae that are occasionally occurring in marine and freshwater bodies throughout the world produce toxins, so called phycotoxins. Some of them like domoic acid, saxitoxin (paralytic shellfish poisoning or PSP toxin), and brevetoxin are of significant human health concern since they may bio accumulate or are magnified in the food chain by fish and shellfish. Occurrence of cyanobacterial toxins (including anatoxins, microcystins, and nodularins) in drinking water represents another hazard to be considered.

Food safety issues

Considering severity, incidence and onset of biological symptoms induced, the risk to health of various forborne hazards, the six principal categories, ranging from greatest to least, are typically ranked by scientists as follows:

1. Microbial contaminants.
2. Nutritional imbalance (excess and deficiency).
3. Environmental contaminants.
4. Natural toxicants.
5. Pesticide residues.
6. Food additives.

It should be noted that the ranking of these hazards is not linear, that of environmental contaminants and natural toxicants being about 1/1000th that of nutrient imbalance and pesticide residues and food additives being about 1/100th that of natural toxicants.

While relatively comprehensive information on risk associated with dietary intake of major classes of mycotoxins and some phycotoxins is available and directives regulating occurrence of these toxic compounds in foods/feeds have been applied in most countries, the situation in the field of natural toxins is more complicated. Therefore in following paragraph only the latter group of natural toxins is discussed in a greater detail.

Hazard related to plant toxins

In one of its papers[2] mentioned in Introduction there was calculated that 99.99 % (by weight) of the pesticides in the American diet are chemicals that plants produce to defend themselves. The rather surprising fact was that at that time (early 90th) only 52 natural pesticides had been tested in high-dose animal cancer tests, and about half (all of them shown to be present in many common foods) were found to be rodent carcinogens. It was concluded that natural and synthetic chemicals are equally likely to be positive in animal cancer tests. It was also concluded that at the low doses of most human exposures the comparative hazards of synthetic pesticide residues are insignificant.

In a practical WHO guide[7] to basic principles and practices aimed at reducing the incidence of food borne illness at both family and community levels following examples of intrinsic chemical hazards associated with intake of some (in particular region) staple food are listed.

Oxalic acid (rhubarb, spinach),
alkaloids
– solanine (potatoes)
– dioscorine (yams),
cyanide (cassava, lima beans),
haemagglutin (red kidney beans),
protease inhibitors (legumes),
phytic acid (bran).

It should be noted that in many cases a failure to recognize the significance of certain traditional food processing/cooking procedures can lead to food safety problems. Cassava, haemaglutins as well as protein inhibitors are typical examples of food commodities that have to be carefully treated before consumption to achieve detoxification. Thermal breakdown of parent compounds, their evaporation or leaching from crop are common mechanisms leading to reduction of their content[9].

There are of course several other conditions under which plant toxins may penetrate into human food chain[5]. For instance contamination of non-toxic raw materials of plant origin with a poisonous non-nutritive plant species such as black nightshade (*Solanum nigrum*) may occur. By accident and other green (unripe) berries of this weed may contaminate peas, beans and other similar crops. According to other scenario raw material of animal origin, mainly fish and milk can become contaminated if the animal has been fed by organisms/plants containing natural toxins. For instance tremetone contained in weeds such as wide snakeroot (*Polygonum*) and/or rayless goldenrod (*Salidago*) can be transferred into milk of grazing cows. Pyrrolizidine alkaloids[9], hepatotoxic and even carcinogenic natural substances occurring in 3 % of world's flowering plants (mainly *Boraginaceae, Compositae,* and *Leguminosae* families) can be transferred into human diet through both the above ways. In addition, some plants such as comfrey (*Symphytum*) have been used as „all-cured“ traditional remedy (official pharmacopoeia) in many cultures for ages. The recent concerns are mainly focused on production of food supplements and herbal teas containing these medicinal herbs

To evaluate/regulate compounds that might be responsible for food poisoning, complex information on all the related aspects has to be available. Unfortunately, as regards natural plant toxins only very limited data are available. In their comprehensive review Essers et al.[10] concluded that contrary to pesticide residues and food additives, the ADI (Acceptable Daily Intake) concept is not applicable for risk management and regulation of food plant toxins. Typically narrow margin between their actual intake and potentially toxic levels would prohibit the use of particular food as far as default uncertainty factors used to establish ADI are applied. As emphasized by experts group the presence of inherent toxins, their bioavailability from matrix and interaction with other inherent plant constituents has to be evaluated together with potential health beneficial effects of the whole food (antioxidants and other natural protective agents can be present).

Regarding the regulatory aspects related to inherent plant toxins, the main problem encountered in this area is, as already mentioned, the lack of essential data on toxicological properties and information on occurrence of these substances in human diet. Establishing maximum levels has to be based both on magnitude of the potential public health/safety risk and the capacity of legally enforceable standard to serve an effective risk management function[11]. In setting priorities for research and further evaluation, various criteria are considered. More than acute risk, the data (both experimental and epidemiological) on chronic toxicity are important in this context. Compounds assumed to be associated with high consumers' exposure in particular region are of concern. Specific risk groups should to be taken into account as well.

Conclusions

Human diet may contain not only residues of various xenobiotics but also natural constituents that are intrinsically toxic. Regarding the plant toxins contained in food crops despite of continual exposure, the risk for consumers is considered relatively small. Besides of adverse health effects these compounds may also exhibit antimutagenic, anticarcinogenic, and antifungal effects. Carcinogenic effects may not be expressed due to small doses or inhibitory effects of other compounds contained in food.

However, under certain circumstances listed below the dietary intake of natural toxins may pose a problem for consumers:

Food commodity is consumed in normal amounts, however due to some inborn error of metabolism adverse reactions occur.

Food constituent is eaten in normal amounts by an individual with abnormal sensitivity such as an allergy.

Common food commodity is consumed in abnormal amounts so that toxicity results.

Abnormal food commodity is consumed in normal amounts.

In any case the greater the variety of food eaten, the less chance of digesting toxins at dangerous levels.

REFERENCES

1. van Egmont H. P: Anal. Bioanal. Chem. *378*, 1152. (2004).
2. Ames B. N., Profet M. and Gold L. S.: Proc. Natl. Acad. Sci. USA *87*, 7777 (1990)
3. Singh B. R. and Tu A. T. (Eds.): Natural toxins 2: Structure, Mechanism of Action and Detection, Kluwer Academic Publishers, (1996).
4. Tu A. T. and Gaffeld W. (Eds.): Natural and Selected Toxins: Biological Implications, ACS Symposium Series, No. 745, (2000).
5. O'Mello J. P. F. (Ed.): Food Safety Contaminants and Toxins, Wallingford, Oxon, (2003).
6. Rosa E., Rosner H., Andrade J., Gevers E., Hallikainen A., Hedley S., Holm S., Lambein F., Laursen P., Strigl A., Sřrensen H. and Vidal-Valverde C.: NETTOX List of Food Plant Toxicants Report No. 1, Danish Vetrinary and Food Administration, (1998)
7. Adams M., Motarjemi Y. (Eds): Basic Food Safety for Health Workers, WHO/SDE/PHE/FOS/99.1, Geneva, (1999).
8. Davídek J. (Ed.): Natural Toxic Compounds of Foods: Formationand Change During Food Processing and Storage., CRC Press, Boca Raton, (1995)
9. Zhou S., Koh H.-L., Gao Y., Gong Z.-Y. and Lee E. J. D.: Life Sci. *74*, 915 (2004).
10. Essers A. J. A., Alink G. M., Speijer G. J. A., Alexander J., Bouwmeister P.-J., van den Brandt P. A., Ciere S., Gry J., Herrman J., Kuiper H. A., Mortby E., Renwick A. G., Shrimpton D. H., Vainio H., Vittozi L. and Koeman J. H.: Environ. Toxicol. Pharmacol. *5*, 155 (1998).
11. Abbott P., Baines J., Fox P., Graf L., Kelly L., Stanley G., Tomaska L.: Food Control *14*, 383 (2003).

L03 ROLE OF PLASMA IN SURFACE AND INTERFACE TECHNOLOGY

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Introduction

Our dreams in this century are the enrichment of our lives, in other words, fulfilling ourselves in our lives with satisfaction. So that, "Health", "Information", and "Environment" are the key words for us in the 21st century.

Material technology made a good progress to pursuit the three key elements in the field of new business. For example, artificial organs such as blood vessels, heart, liver, bone are for "Health"; flat panel display, flexible and plastic display, and plastic IC are for "Information"; and biodegradable plastics such as polylactic acid are for "Environment". Development of such new materials is an important factor to realize new life, however, never satisfies yet all requests from the society. New materials in this century should harmonize their properties always with environment where they operate. For example, artificial blood vessels are the tube of plastics for traveling blood, not as the same as water pipes. Surfaces of the artificial blood vessels contact always with blood, and should evade from adhesion of thrombi. It is an important issue that how to modify surfaces of the materials in order to harmonize with environments. This is called as the surface or interface technology. The chemical and physical structure of the surface or interface should be controlled in a nano-size scale for the harmonization.

Plasma is a useful tool for modifying surface and interface of plastic materials. Plasma contains electrons, ions, and radicals that can make modification reactions on the polymer surfaces and interfaces. This modification process is called as "Plasma Treatment", and is restricted in the topmost layer of the materials. Plasma treatment changes drastically properties of the surface but never changes bulk properties of the materials. Many investigators have focused on the surface modification of plastic materials by plasma especially in order to make composite materials with good performance. Flexible printed circuit board, FPC, is a composite material of copper metal layer and polymer films such as polyimide and liquid crystal polyester films. Copper metal is deposited on the film surfaces by vacuum deposition, sputtering, and ion plating techniques. In this composite, an importance issue is how to adhere copper metal with polymeric film surface. In this paper, we focus on how to harmonize interface between polymeric films and copper metal layer in adhesion.

Table I
Peel strength for polyimide/metal adhesives joints

Metals	Peel strength [gf mm^{-1}]
Au	31
Cu	73
Ni	86
Cr	117

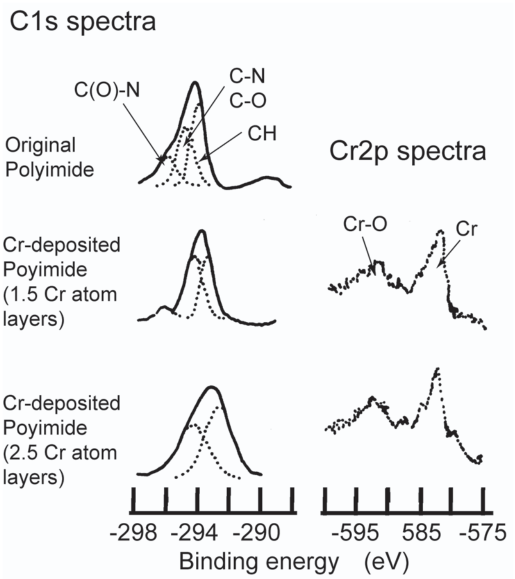

Fig. 1a. **XPS (C1s and Cr2p) spectra for Cr-deposited polyimide film surfaces**

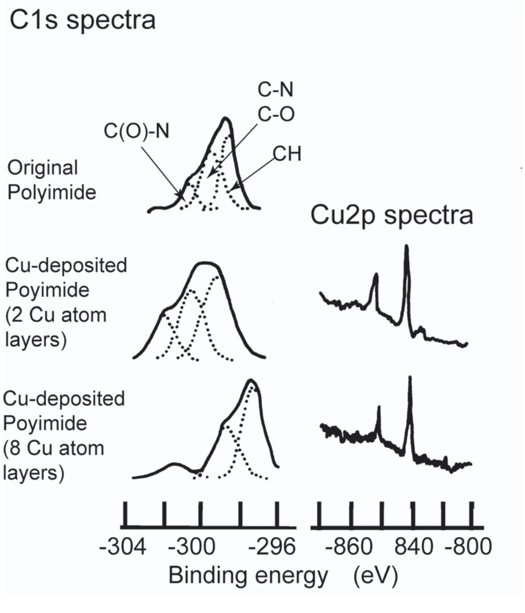

Fig. 1b. **XPS (C1s and Cu2p) spectra for Cu-deposited polyimide film surfaces**

Interactions at Interface between Polyimide Film and Copper Metal Layer

When copper metal deposit on polyimide film surface, some interactions occur at the interface between the copper metal and polyimide film to get strong adhesion. The interactions involve mechanical interlock (anchor effects), chemical bonding, static-electrical force, etc. The interaction due to chemical bonding is most important way to harmonize interface between polymer surface and deposited copper metal. Kim et al.[1] discussed on what metals adhered strongly to copper metal. Table I shows the peel strength (90 degrees direction) of polyimide/metal adhesive joints. The peel strength depended strongly on what metal deposited on the film surfaces. Chromium metal deposited on polyimide film surfaces showed a high peel strength of 117 gf mm^{-1}, and copper metal showed a low peel strength of 73 gf mm^{-1}, which was about 60 % of the chromium metal/polyimide joints. This comparison indicates some chemical interactions occurred at the interface between polyimide surface and chromium metal.

Chou et al.[2] investigated on what chemical interactions occurred between polyimide surface and chromium or copper metal using XPS. Fig. 1a and 1b show C1s, Cr2p or Cu2p spectra for the Cr-deposited and Cu-deposited polyimide surfaces. C1s spectrum for the original polyimide surface was decomposed into three components, CH, C–O and C–N, and C(O)N groups. When chromium metal (1.5 Cr atom layer) was deposited on the polyimide surfaces, the C1s spectrum for Cr-deposited polyimide, as shown in Fig. 1a, showed distinguished changes compared with the original C1s spectrum. Amide, C(O)N, groups in the polyimide chains was diminished, and new Cr–O group appeared in the Cr2p spectra (Fig. 1a). On the other hand, even when copper metal (deposition of 2 Cu atoms layer) was deposited on the polyimide film surface, there was distinguished decrease in amide groups in the polyimide chains, and also no Cu–O group appeared (Fig. 1b). From these spectral results, we believe that the metal–O–C bond formation at the interface between polyimide film and metal layer is a key factor to make good adhesion between polyimide and metals.

Surface Modification of Polyimide Films for Adhesion with Copper Metal by plasma

To make good adhesion between polyimide film and copper metal, some functional groups which could interact with copper metal layer were formed on the polyimide film surfaces. Inagaki et al.[3] used plasma treatment for formation of oxygen functional groups on the polyimide film surfaces. XPS spectra for the plasma-treated polyimide films showed formation of carboxyl groups on the film surfaces. Peel strength of the plasma-treated polyimide film/copper metal was improved from 0.73 N/10 mm to 2.9 N/10 mm by the Ar plasma treatment (Table II). Paik and Ruoff[4] tried oxygen ion beam technique for surface modification of polyimide films.

Table II
Effects of plasma treatments on peel strength for polyimide/copper metal adhesives joints

Plasma	Peel strength [N/10 mm]
None	0.73 ± 0.06
Ar	2.9 ± 0.09
N_2	2.2 ± 0.09
NO	2.2 ± 0.01
NO_2	2.1 ± 0.08
CO	1.2 ± 0.06
CO_2	1.2 ± 0.01
O_2	1.2 ± 0.16

Nitrogen functional groups also have capability to make good interaction with copper metal. Nitrogen functional groups were introduced on polyimide film surfaces by plasma techniques such as plasma graft copolymerization, silane coupling reactions, etc. Table III summarizes improvement in the peel strength by the plasma treatment, plasma graft copolymerization, and silane coupling reactions. Chemicals used for the silane coupling reactions are shown in Fig. 2. The peel strength was increased from 0.94 N/5 mm to 3.2 N/5 mm in the case of plasma graft copolymerization of vinyl imidazole.

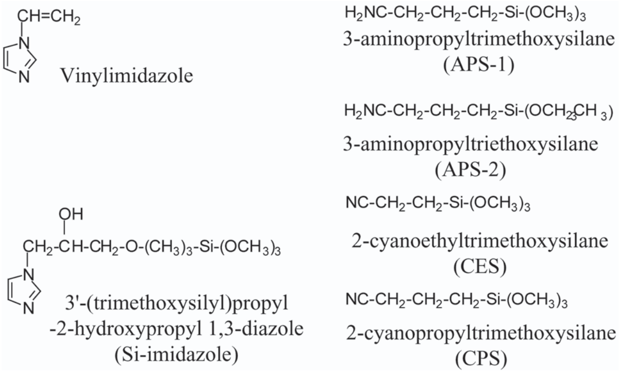

Fig. 2. **Chemicals used for silane coupling reactions**

Silane coupling reactions using imidazole and cyano groups-containing silanes also were useful way to improve adhesion with copper metal. The failure mode of the peeling changed from at the interface between the polyimide film and copper metal layer (in the case of the original polyimide film) to at the inner layer of the polyimide films (in the cases of the Ar plasma-modified, plasma graft-copolymerized, and silane-couplinged films). This change in the failure mode indicates that the strong adhesion between polyimide film and copper metal layer was accomplished by the plasma-assisted modifications such as Ar plasma treatment, plasma graft-copolymerization, and silane coupling reactions.

Kang[5] and Kim[6] separately have proposed other plasma-assisted modification. Firstly, polyimde film surfaces were exposed to Ar plasma to form radicals on the film surfaces, and then graft-copolymerized with nitrogen-containing vinyl monomers such as vinylimidazole and vinylpyridine under UV irradiation. Essentially, this modification technique is the same as the plasma graft copolymerization technique except UV irradiation at the same time that the graft copolymerization reactions proceed. Kim also proposed another technique to improve the adhesion. Copolymers with both imidazole and methoxy silyl groups were blended with polyimide to modify properties of film surfaces. Besides of these plasma-assisted modifications, there are many other techniques of surface modification for adhesion between polyimide film and copper metal (see Appendix).

Surface Modification of Liquid Crystal Polyester Film for Copper Metallization

Poly(oxybenzoate-co-oxynaphthoate) is called liquid crystal polyester, LCP, because of thermotropic liquid-crystalline properties. LCP possesses excellent physical, chemical, and mechanical properties, and its electrical properties such as low dielectric constant and loss also are superior to those of polyimide. These advantages of LCP can expand its application to new fields such as flexible printed circuit boards, encapsulating ICs, etc. From this aspect, copper metallization of LCP also is one of interesting topics in the field of surface and interface technologies. Similarly in the case of the copper metallization of polyimide films, oxygen

Table III
Peel strength for modified polyimide/copper metal adhesives joints and their failure modes

Surface modification	Reagents for	Peel strength	Failure mode of adhesive joint
None	None	0.94	Interface between polyimide and copper metal
Ar plasma treatment	Ar plasma	1.5	Inner layer of Ar plasma-modified polyimide layer
Graft copolymerization	Vinyl imidazole	3.2	Inner layer of polyimide film
Silane coupling	Si-imidazole	2.1	Inner layer of silane-coupled layer
	APS-1	0.89	Interface between polyimide and copper metal
	APS-2	0.90	Interface between polyimide and copper metal
	CES	2.2	Inner layer of silane-coupled layer
	CPS	2.3	Inner layer of silane-coupled layer

and nitrogen functionalities formed on the LCP surfaces may contribute to adhesion with copper metal layer. LCP film surfaces were treated with NH_3, N_2, O_2, and Ar plasmas, and the film surfaces were metallized by a combination of evaporation and electroplating processes. The adhesion between the deposited copper layer and the LCP surface was evaluated in terms of peel strength. Fig. 3. shows typical peel strength results as functions of plasma exposure time and plasma gas used for the modification.[7] The peel strength increased from 0.03 to 0.4–1.4 N/5 mm with increasing plasma exposure time, and leveled off at a plasma exposure time of 60 s. At an exposure time of 60 s, the peel strength was in the order: NH_3 plasma (1.4 N/5 mm) > N_2 plasma (1.1 N/5 mm) > O_2 plasma (0.8 N/5 mm) > Ar plasma (0.4 N/5 mm). The NH_3 plasma was most effective in improvement of the adhesion. Furthermore, a plasma exposure time of more than 60 s was necessary to improve the adhesion.

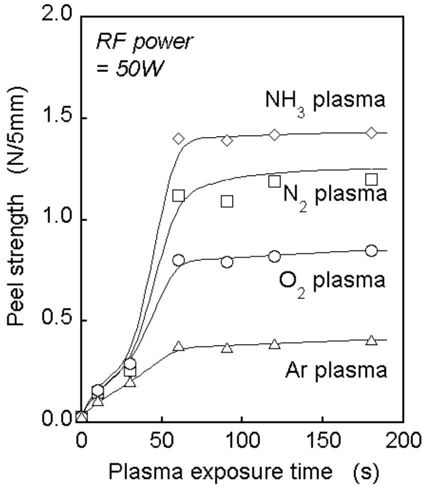

Fig. 3. **Peel strength for plasma-modified polyimide film/copper metal adhesive joints as functions of plasma and plasma exposure time**

The peel strengths between the copper metal and the plasma-modified LCP, as shown in Fig. 3., were 1.4 N/5 mm for the NH_3 plasma-modified LCP surfaces and 0.41 N/5 mm for the Ar plasma-modified surfaces. There is a large difference in peel strength between the NH_3 plasma-modified and Ar plasma-modified LCP surfaces. The NH_3 plasma-modified LCP surface has good adhesion with copper metal, but the Ar plasma-modified surface has poor adhesion. "Is there any difference between the NH_3 and Ar plasma-modified LCP surfaces?" We expect that XPS can answer the question. XPS (C1s, O1s, and N1s) spectra were recorded at a take-off angle of 20 degrees against the LCP surface. Fig. 4a and 4b show C1s, O1s, and N1s spectra for the NH_3 plasma- and Ar plasmas-modified LCP surfaces. The original LCP surface showed a complex C_{1S} spectrum decomposed into four components at 285.0, (C1s component #1) 286.5 (C1s component #2), 289.3 (C1s component #4), and 291.9 eV (C1s component #5). These components are assigned to CH, C–O, C(O)–O, and π–π* shake-up satellite, respectively. The C1s spectrum for the NH_3 plasma-modified LCP surface was quite different from that for the original LCP surface. In the C1s spectrum, the peak due to C(O)–O became less intense, and the peak due to π–π* shake-up satellite disappeared. A new component #3 due to C=O (ketone type) appeared at 287.8 eV. This spectrum indicates that NH_3 plasma exposure caused breakdown of a part of the C(O) groups in ester linkages and formed C=O groups of ketone type. The Ar plasma-modified LCP surface showed unique C1s spectrum that was quite different from the original as well as the NH_3 plasma-modified LCP surfaces. The C1s spectrum for the Ar plasma-modified LCP surface consisted of four C1s components: C1s component #1, C1s component #2, C1s component #3, and the C1s component #4. There is no large difference in the C1s components between the NH_3 and Ar plasma-modified LCP surfaces, although the C1s component #5 due to π–π* shake-up satellite was not observed on the NH_3 plasma-modified LCP surface, but on the Ar plasma-modified LCP surface. The NH_3 and Ar plasma modifications led to degradation of C(O)–O in ester linkages and to formation of C=O of ketone type.

The O1s spectrum for the original LCP surface, as shown in Fig. 4b, contained two peaks, which appeared at 531.2 and 533.0 eV. The peaks were assigned to O=C (O_{1s} component #1) and O–C (O_{1s} component #2), respectively. The relative concentrations of the components # 1 and #2 were 53 and 47%, respectively, which corresponded to those (50 and 50%) calculated from the repeat unit of LCP polymer. The NH_3 and Ar plasma-modified LCP surfaces showed O_{1s} spectra that were different from that for the original LCP surface. The spectra were decomposed into two components, O_{1s} components #1 and #2, which were assigned to O=C in ester and carbonyl groups (at 531.2–531.6 eV) and O–C in ester and hydroxyl groups (532.0–532.9 eV), respectively. Furthermore, the NH_3 plasma modification led to a new N1s spectrum (Fig. 4b). The spectrum was decomposed into two components, N_{1s} components #1 and #2, which were assigned to N–C=O in amide groups at 399.5 eV and NH in amino groups at 401.1 eV, respectively.

The differences in the XPS spectra between the NH_3 and Ar plasma-modified LCP surfaces are the disappearance of the π–π* shake-up satellite (C1s component #5) and the formation of nitrogen groups such as amide and amino groups (N1s components #1 and #2) in the NH_3 plasma modified surfaces. Except for these differences, the two plasma-modified LCP surfaces resemble each other in chemical composition. Do amide or amino groups formed on the LCP surfaces by the NH_3 plasma contribute to the adhesion? We have already investigated what nitrogen-containing groups contributed to the adhesion with copper metal. Our conclusion from the investigation is that imidazole and cyano groups interact with copper metal and contribute to the adhesion, but amino groups contribute only marginally. On the contrary, some investigators[8] pointed out that amino groups also interacted

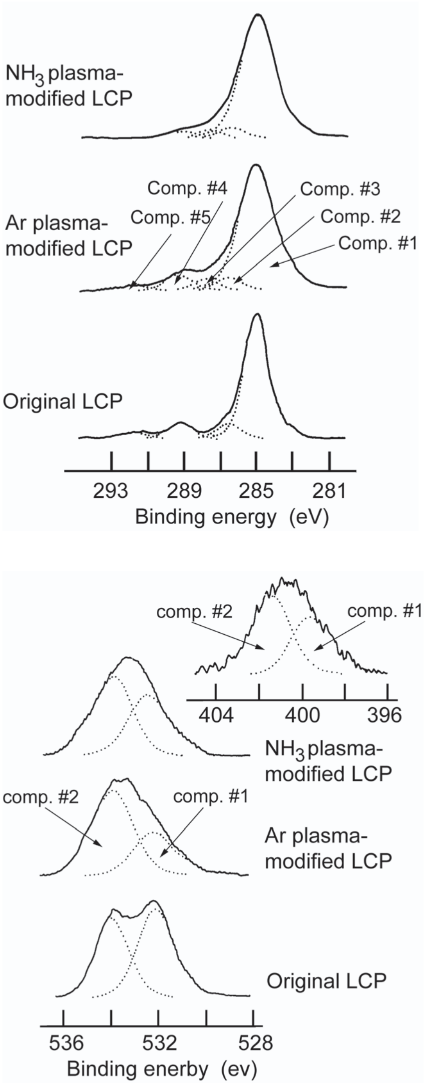

Fig. 4. **C1s, O1s, and N1s spectra for the NH_3 plasma- and Ar plasmas-modified LCP surfaces**

with copper metal, although they did not say whether the interaction could contribute to the adhesion. At the present time, we can not conclude whether amino groups contribute strongly to adhesion with copper metal or not.

Conclusion

How useful plasma is for modifying surface and interface of polymeric materials is demonstrated in the case of polyimide/copper metal joint and liquid crystal polyester/copper metal joint. Flexible printed circuit board, FPC, is a composite material of copper metal layer and polymer films such as polyimide and liquid crystal polyester, LCP, films. Copper metal is deposited on these film surfaces by a combination of vacuum deposition and electroplating.

The strong adhesion between polyimide or LCP film and copper metal layer was accomplished by the plasma-assisted modifications such as NH_3 plasma treatment, plasma graft-copolymerization of nitrogen-containing vinylmonomers, and nitrogen-containing silane coupling reactions. These improved adhesions showed how effectively plasma operated in the surface modification process.

REFERENCES

1. Kim Y. –H., Kim J., Walker G. F., Feger C., Kowalczyk S. P.: J. Adhesion Sci. Technol., *2*, 95 (1988).
2. Chou N. J., Tang C. H.: J. Vac. Sci. Technol., *A2*, 751 (1984).
3. Inagaki N., Tasaka S., Hibi K.: J. Adhesion Sci. Technol., *8*, 395 (1994).
4. Paik K. W., Ruoff A. L.: J. Adhesion Sci. Technol., *4*, 465 (1990).
5. Yang G. H., Kang E. T., Neoh K. G., Zhang Y., Tan K. L.: Colloid Polymer Sci., *279*, 745 (2001).
6. Jang J., Jang I., Kim H.: J. Adhesion Sci. Technol., *12*, 323 (1998).
7. Inagaki N., Park Y. W., Narushima K., Miyazaki K.: J. Adhesion Sci. Technol., *18*, 1427 (2004).
8. Nowak S., Colland M., Dietler G., Schmutz P., Schlapbach L.: Surf. Interf. Anal., *20*, 416 (1993).

APPENDIX

Surface modification techniques of polyimide films for adhesion with copper metal are summarized as follows:

1. Mack R. G., Grossman E., W. N. Unertl: “Interaction of Copper with a Vapor Deposited Polyimide Film”, J. Vac. Sci. Technol., *A8*, 3827 (1990).
2. Galuska A. A.: “Adhesion Enhancement of Ni Films on Polyimide using Ion Processing. I. $^{28}Si^{+}$ Implantation”, J. Vac. Sci. Technol., *B8*, 470 (1990).
3. Galuska A. A.: “Adhesion Enhancement of Ni Films on Polyimide using Ion Processing. II. $^{84}Kr^{+}$ Implantation”, J. Vac. Sci. Technol., *B8*, 482 (1990).
4. Hiraoka H., Lazare S.: “Surface Modification of Kapton and cured Polyimide Films by ArF Excimer Laser: Application to Imagewise Wetting and Metallization”, Applied Surf. Sci., *46*, 264 (1990).
5. Ulmer G., Hasselberger B., Busmann H. G., Campbell E. E. B.: “Excimer Laser Ablation of Polyimide”, Applied Surf. Sci., *46*, 272 (1990).
6. Oh T. S., Kowalczyk S. P., Hunt D. J., Kim J.: “Adhesion Enhancement of Cr/Polyimide Interface using RF Pre-sputtering of Polyimide Surfaces”, J. Adhesion Sci. Technol., *4*, 119 (1990).
7. Paik K. W., Ruoff A. L.: “Adhesion Enhancement of Thin Copper Film on Polyimide Modified by Oxygen Reactive Ion Beam Etching”, J. Adhesion Sci. Technol., *4*, 465 (1990).
8. Shin D.-Y., Klymko N., Flitsch R., Paraszczak J., Nunes S.: “Oxygen induced Adhesion Degradation of Metal/Polyimide Interface”, J. Vac. Sci. Technol., *A9*, 2963 (1991).

9. Paik K. W., Cole H. S., Saia R. J., Chera J. J.: "Studies on Metal/Benzocyclobutene Interface and Adhesion", J. Adhesion Sci. Technol., *7*, 403 (1993).
10. Inagaki N., Tasaka S., Hibi K.: "Improved Adhesion between Plasma-treated Polyimide Film and Evaporated Copper", J. Adhesion Sci. Technol., *8*, 395 (1994).
11. Ma J. B., Dragon J., van Derveer W., Entenberg A., Lindberg V., Anschel M., Shih D. Y., Lauro P.: "Use of High Temperature and High Humidity to Test the Adhesion of Sputtered Copper to a Polyimide Surface modified by an AC Nitrogen Glow Discharge", J. Adhesion Sci. Technol., *9*, 487 (1995).
12. Lee K. –W., Walker G. F., Viehbeck A.: "Formation of Polyimide-Cu Complexes: Improvement of Direct Cu-on PI and PI-on-Cu Adhesion", J. Adhesion Sci. Technol., *9*, 1125 (1995).
13. Inagaki N., Tasaka S., Masumoto M.: "Plasma Graft Polymerization of Vinylimidazole onto Kapton Films Surface for Improvement of Adhesion between Kapton Film and Copper", J. Appl. Polymer Sci., *56*, 135 (1995).
14. Inagaki N., Tasaka S., Masumoto M.: "Improved Adhesion between Kapton Film and Copper Metal by Plasma Graft Polymerization of Vinylimidazole", Macromolecules, *29*, 1642 (1996).
15. Rozovskis G., Vinkevicius J., Jaciauskiene J.: "Plasma Surface Modification of Polyimide for Improving Adhesion to Electroless Copper Coatings", J. Adhesion Sci. Technol., *10*, 399 (1996).
16. Iwamori S., Miyashita T., Fukuda S., Nozaki S., Fukuda N., Sudoh K.: "Changes in the Peeled Surfaces of Copper Thin Films deposited on Polyimide Substrates after Heat Treatment", J. Adhesion, *63*, 309 (1997).
17. Ghosh I., Konar J., Bhowmick A. K.: "Surface Properties of Chemically Modified Polyimide Films", J. Adhesion Sci. Technol., *11*, 877 (1997).
18. Iwamori S., Miyashita T., Fukuda S., Fukuda N., Sudoh K.: "Effect of a Metallic Interfacial Layer on Peel Strength Deterioration between a Cu Thin Film and a Polyimide Substrate", J. Vac. Sci. Technol., *B15*, 53 (1997).
19. Ang A. K. S., Kang E. T., Neoh K. G., Tan K. L., Cui C. Q., Lim T. B.: "Low-temperature Thermal Graft Copolymerization of 1-Vinyl Imidazole on Polyimide Films with simultaneous Lamination to Copper Foils", J. Adhesion Sci. Technol., *12*, 889 (1998).
20. Jang J., Jang I., Kim H.: "Effect of the Mole Ratios of Silane-modified Polyvinylimidazoles on Adhesion Promotion of the Polyimide/Copper System", J. Adhesion Sci. Technol., *12*, 323 (1998).
21. Jang J., Jang I., Kim H.: "Adhesion Promotion of the Polyimide-Copper Interface using Silane-modifiec Polyvinylimidazoles", J. Appl. Polym. Sci., *68*, 1343 (1998).
22. Kim H., Jang J.: "Effect of Copolymer Composition in Vinyl Silane modified Polyvinylimidazole on Copper Corrosion Protection at elevated Temperature", Polymer, *39*, 4065 (1998).
23. Inagaki N., Tasaka S., Onodera A.: "Improved Adhesion between Kapton Film and Copper Metal by Sinae--coupling Reactions", J. Appl. Polymer Sci., *73*, 1645 (1999).
24. Ang A. K. S., Liaw B. Y., Kiaw D. J., Kang E. T., Neoh K. G.: "Low-temperature Thermal Graft Copolymerization of 1-Vinyl Imidazole on Fluorinated Polyimide Films with simultaneous Lamination to Copper Foils", J. Appl. Polym. Sci., *74*, 1478 (1999).
25. Kim H., Jang J.: "Interfacial Behavior of Polyimide/Primer/Copper System by Preoxidation of the Primer", J. App Primer", J. Appl. Polym. Sci., *78*, 2518 (2000).
26. Ang A. K. S., Kang E. T., Neoh K. G., Tan K. L., Cui C. Q., Lim T. B., "Low-temperature Graft Copolymerization of 1-Vinyl Imidazole on Polyimide Films with simultaneous Lamination to Copper Foils -Effects of Crosslinking Agents", Polymer, *41*, 489 (2000).
27. Inagaki N., Tasaka S., Baba T., "Surface Modification of Polyimide Film Surfaces by Silane Coupling Reactions for Copper Metallization", J. Adhesion Sci. Technol., *15*, 749 (2001).
28. Yang G. H., Kang E. T., Neoh K. G., Zhang Y., Tan K. L.: "Electroless Deposition of Copper on Polyimide Films Modified by Surface Graft Copolymerization with Nitrogen-containing Vinyl Monomers", Collid Polym. Sci., *279*, 745 (2001).
29. Zhang Y., Kang E. T., Neoh K. G., Huang W., Huan A. C. H., Zhang H., Lamb R. N.: "Surface Modification of Polyimide Films via Plasma Polymerization and Deposition of Allylpentafluorobenzene", Polymer, *43*, 7279 (2002).
30. Wang W. C., Kang E. T., Neoh K. G.: "Electroless Plating of Copper on Polyimide Films modified by Plasma Graft Copolymerization with 4-Vinylpyridiene", Applied Surf. Sci., *199*, 52 (2002).
31. Inagaki N., Park Y. W., Narushima K., Miyazaki K.: "Plasma Modification of Poly(oxybenzoate-co-oxynaphthoate) Film Surfaces for Copper Metallization", J. Adhesion Sci. Technol., *18*, 1427 (2004).

L04 FROM CONCENTRATIONS TO MASS FLUXES. AN ANALYTICAL CHEMIST'S VIEW OF BRIDGING ECONOMY AND ECOLOGY

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Man and his environment

Man is he most highly developed living being on our planet and at the same time the most sensitive part of the ecosystem Earth. He is part of the biosphere and as such exposed to many influences of the surrounding compartments atmosphere, hydrosphere, and pedosphere (Fig. 1.).

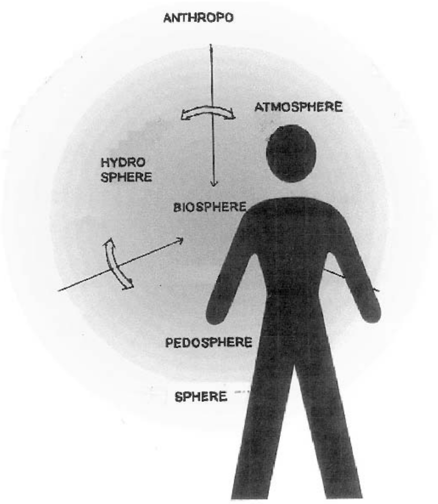

Fig. 1. **Man and his physical environment**

On the other hand, however, he is strongly affecting his environment through the many civilizatory activities necessary to establish his "habitat" and to guarantee his survival (anthroposphere, Fig. 1.).

This complex interactive system of environmental compartments is based on a large variety of material and energy fluxes. In this context the anthroposphere, representing man's civilizatory status, is of utmost relevance for changes of the terrestrial ecosystem and therefore the major item in all discussions on how to protect our environment.

The role of analytical chemistry: Surveying technical progress and controlling risks connected with it

Through more than 200 years analytical chemistry almost exclusively served as a means to discover and describe step by step our material environment and with these goals achieved great triumphs, as for instance the finding of new elements, the determination of the composition of milligram amounts of organic substances, or the discovery of the nuclear fission of uranium.

During the second half of the 20th century not only the methodological spectrum of analytical chemistry but also its fields of application – e. g. clinical analysis, industrial production, environmental control, material science – have dramatically expanded. Therefore its role as a reliable partner of a wide variety of different disciplines can only be fulfilled after establishment of new experimental strategies. In this context the conventional *static* material characterization has to be supplemented by a *dynamic* investigation and control of processes leading to certain products or changing their properties. This aspect of analytical chemistry in particular opens the way from the measurement of concentrations to the quantification of mass fluxes. It has already found substantial application in industrial process analysis and is entering other fields of human activities too. It certainly has a specially close relation to all efforts focussed on maintaining the terrestrial ecosystem hospitable to life.

Industrial and environmental measurements

It is short-sighted to look at industrial enterprises only as sources that release unfavourable matter to the environment. Industrial production is also a strong factor of economic welfare of a nation, This conflicting situation may be overcome with the expertise of analytical chemistry offering the tools for industrial *and* environmental process analysis. The Tables I and II show that the *mass flux concept* is of equal relevance for both areas.

Table I
Motivation for and Goals of Industrial Process Analysis

- Minimization of Raw Material Input
- Increase of Product Yield
- Improvement of Product Quality
- Assurance of Product Identity
- Minimization of Discharge of Waste and Pollutants

- **Summing up: Decrease of Costs, Increase of Profit**

Table II
Motivation for and Goals of Environmental Measurements

- Control of Technical Measures for Reduction of the Release of Pollutants
- Establishment of Foundations for Exposure Assessment (pollution survey, dispersion of pollutants, localization of emission sources, work place control)
- Solution of Problems with Interdisciplinary Character (global trends, global mass balances, natural vs. anthropogenic sources of pollutants, transport modelling, physical and (bio) chemical processes, source receptor relationships, dose-response relationships)

It is obvious that, for instance, the last entry of Table I and the first one of Table II make a link between industrial and environmental process analysis. This link has to be made much stronger than it presently is, in order to connect good economy with satisfactory environmental quality.

How to measure and where to measure

The investigation and control of processes require methods capable to adequately describe and quantify the physicochemical or biological changes occurring in a compartment under study as a function of time. A fundamental requirement is the matching of the characteristic time of the analyte signal generation with the characteristic time of change caused by transport and/or chemical conversion in the process investigated. Terms such as "monitoring", "on-line", "in-situ", or "real-time" are often used to distinguish process related dynamic techniques from material characterizing static ones.

In environmental studies, ambient air, workplace atmospheres, and surface waters are typical compartments for application of such dynamic techniques. Furthermore transport and transformation in biological systems and industrial production with the control of the inherent release of waste gas and waste water are relevant targets for *process related analytical chemistry* (PREACH). A good example for how to involve PREACH in a multidisciplinary study of an industrial environment has been the “Serra do Mar” project carried out at Cubatão, State of São Paulo, Brazil[1].

Conclusion

Both, industrial production and environmental processes are connected to chemical mass fluxes. Their sufficiently fast quantification is of greatest advantage for cutting down production costs and improving product quality at the one hand, and for reducing discharges of pollutants to the environment at the other. Consequently, the establishment of a broad band methodology capable to measure mass fluxes is an important matter of research for analytical chemists during the forthcoming years

REFERENCES

1. Klockow D., Targa H. J.: Pure & Appl. Chem. *70*, 2287 (1998).

L05 SELF-ORGANIZATION OF CRYSTALLITES IN GEL PHASES

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Abstract

Self-organization of solid mineral particles of silver halides prepared by precipitation in a gel-like phase of water soluble cellulose derivative has been studied. There was found that development of microscopic scale dimension aggregates is strongly dependent on initial concentration of the original precursors, temperature of the process, and initial concentration of electrolytes and tensides. The prepared crystallic self-organized products are characterized by means of the fractal analysis, optical microscopy, scanning electron microscopy, and DTG method.

Introduction

Organic-inorganic hybrids with well-defined morphology and structure, at the micro- and nano-metric scale, represent a very interesting class of materials both for their use in different branches of technology and in the theoretical studies of unique processes of biomimetic composites preparation[1].

Ordered molecular clusters are currently attracting wide attention in the physical, chemical and biological sciences. The design and preparation of functional materials such as thin-layered microstructures, reagent films for biosensors, devices for optoelectronics requires knowledge and control of nano- and microarchitectures from the very early stages of self-organization. The requirement touches upon the control of nucleation growth, morphology and structure of crystals, particularly at interphases[2].

This materials with different level of macro- or micro-scopic organization, both natural and man-made, have long been known as a structural components in the case of bones and other endo- and exoskeletal architectures of biological origin, adobe, leather, reinforced plastic and other industrial auxiliary means: In recent years an increasing number of papers and patents have appeared dealing with bulk and more sophisticated micro-structured hybrid materials, focused on synthetic approach or on the specific application. Such interest arises from several unique features of these materials resulting from specific synergetic effects influencing the mechanical, electrical, optical and thermodynamic properties of these hybrids with respect to those of the constituents[3–5].

There is possible to find in the literature several methods for self/organized aggregates preparation[1]. In many cases it is not possible to grow crystals of suitable quality and size using conventional methods starting from melts or solutions. The method of crystal growth in gel is often a very powerful alternative[6,7].

Structural self-organization of particles of a colloid dispersion system can be taken as an evolution of different states of a set of initial structural elements according to I. Prigogine[8] in nonequilibrium systems. Oscillating concentrations and geometrical concentration patterns can be a result of chemical reactions and diffusion, the same dissipative processes that, in a closed system, wipe out inhomogenities and drive the system to a stationary timeless homogenous state of equilibrium.

Experimental

As a model system for the study it has been taken the process of silver halide preparation realized as a precipitation of alkalinous halides with silver nitrate in hydroxyethylcellulose water solutions and following evaporation of solvent in open thin layer under different thermal conditions.

Results and discussion

In Fig. 1.–3. there are given SEM images of the self-organized silver bromide nanometric particles into a higher order crystallites of a micrometric dimension prepared in the same concentration and temperature conditions (the concentration of hydroxyethylcellulose in all given cases was

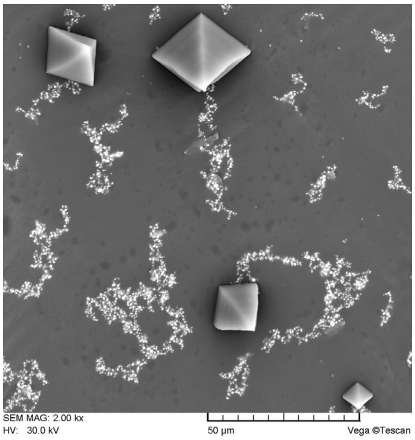

Fig. 1. **SEM image of the self-organized silver bromide nanometric particles prepared in hydroxyethylcellulose and solidification at temperature 100 °C**

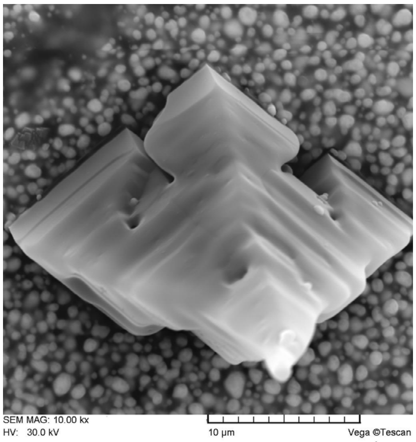

Fig. 2. **SEM image of the self-organized silver bromide nanometric particles prepared in hydroxyethylcellulose and solidification at temperature 100 °C**

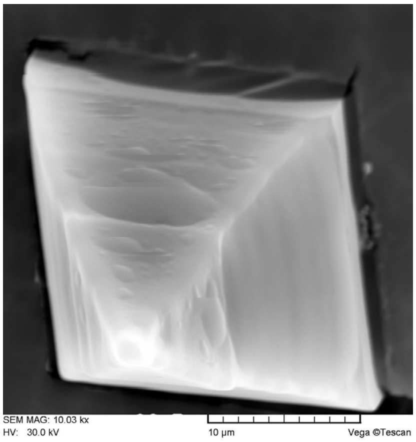

Fig. 3. **SEM image of the self-organized silver bromide nanometric particles prepared in hydroxyethylcellulose and solidification at temperature 100 °C**

1 mass %, and temperature 100 °C). In the Fig. 1. is remarkable development of cubic particles of the merely the same orientation with the vertex normal to the starting surface of the solution. Quite evident dissipation of the cubic structural elements into random linear and cyclic structures proofs that the system was in a strong nonequilibrium state evolving to an ordered state as a result of fluctuations, as “order through fluctuations”[9]. In these nonequilibrium systems, oscillating concentrations and geometrical concentration patterns can be a result of chemical reactions and diffusion mentioned above. According to D. Kondepudi and I. Prigogine[10] for the stability of nonequilibrium stationary state is valid the inequality

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\delta^2 S}{2} = \sum \delta F_\mathrm{k} \delta J_\mathrm{k} > 0 \qquad (1)$$

where F_k and J_k are driven force and the flow of k-component taken in the regard and the other symbols have their usual meaning. The loss of stability of a nonequilibrium state can be analyzed using the general theory of stability for solutions of a nonlinear differential equation.

There is necessary encounter the basic relationship between the loss of stability, multiplicity of solutions and symmetry with special respects to changes of:

concentration of silver halide particles,

total interface energy in the system,

concentration of electrolyte by-products (KNO_3, ...),

temperature as a consequence of water molecules evaporation, and

compression of hydroxyethylcellulose coils of different degree of solvation.

REFERENCES

1. Castelvetro V., Vita C. De.: Adv. Colloid Interface Sci., *108*, 167 (2004).
2. Kuzmenko I., Rapaport H., Krjaer K., Als-Mietsin J., Weissbuch I., Lahav M., Leiserowit L.: Crystalline Architectures at the Air-Liquid Interface: From Nucleation to Engineering. In Soft Condensed Matter: Configuration, Dynamies and Functionality”, Kluwer A. P., Dordrecht, 185–217 (2000) (Skjeltorp A. T. and Edwards S. F., eds.)
3. Ginji T., Makabe Y., Takamura N., Abi Y.: Appl. Organoment. Chem. *15*, 683 (2001).
4. Tissot L., Reymond J. P., Lefebre F., Bourgeat-Lami E.: Chem. Mater. *14*, 1325 (2002).
5. Evmenenko G., Yu C.-J., Kewalramani S., Dutta P.: Polymer *45*, 6269–6273 (2004).
6. Sperka G.: Progr. Colloid Polymer Sci. *77*, 207 (1988).
7. Arora S. K.: Progr. Cryst. Growth Charact. *4*, 345 (1981).
8. Prigogine I.: From Being to Becoming. W. H. Freeman, San-Francisco (1980).
9. Prigogine I., Stengers I.: Order out of Chaos, Bantam, New York (1984).
10. Kondepudi D., Prigogine I.: Modern Thermodynamics, J. Wiley, Chichester (1998).