XPS INVESTIGATIONS ON SOLID SURFACES: RESULTS OBTAINED BY A RECENTLY INSTALLED COMMERCIAL INSTRUMENT

I. BERTÓTI, GY. MINK, A. TÓTH, M. RÉVÉSZ, M. MOHAI and T. SZÉKELY

Research Laboratory for Inorganic Chemistry
of the Hungarian Academy of Sciences, Budapest

Summary

The applicability of the ESCA method and the capability of the recently installed KRATOS XSAM 800 instrument is demonstrated in various fields, e.g. in gas-solid reactions, catalysts and catalysis, layer structures, glass and mineral surfaces and also in the investigation of polymers and coals.

Nowadays the information on the upper atomic layers of solid samples (both chemical composition and structure) is becoming more and more important not only from scientific point of view but also for technical applications. Recently, with the purchase of a KRATOS XSAM800 instrument, a new possibility opened for photoelectron spectroscopic (ESCA) investigations in various areas. In this paper the ability and capacity of the method are attempted to be shown in some examples. Since the work of Siegbahn and coworkers [1] the theoretical basis of the method can be considered well known, and is described also in more recent literature [2–5]. The method is based on the following physical process: the electrons of the inner or the outer shells are excited by X-ray (XPS = X-ray Photoelectron Spectroscopy) or UV (UPS = Ultraviolet Photoelectron Spectroscopy) photons and the kinetic energy of the emitted electrons is measured. As the energy of the exciting photons is known, the ionization or binding energies (B.E. as it became familiar in the English literature) for the atomic levels can be calculated.

As far as the energy levels are characteristic for the constituent elements, determination of B.E. values makes available qualitative analysis. Small shifts of the lines (the so-called chemical shift) depend on the chemical environment and give information about the chemical structure and binding types.

Measuring the peak areas and using the theoretical or experimental cross-section values, the elemental composition of the upper 3–6 nm layer of the surface can be determined with an accuracy of about 5 rel. pct. Information on the deeper layers can be obtained by in situ ion etching. In this case 0.2–1 nm thick layers can be removed step by step by accelerated (1–5 keV) Ar (He, Ne) ions and the characteristic lines are recorded after each etching step. A so-called depth profile is obtained by this way.

Though this technique has been applied for years in the Institute of Nuclear Research of the H.A.S. with a home-constructed instrument and a vast amount of information has been given, the introduction of the present, computer controlled, efficient, third generation instrument has greatly enlarged the possibilities of surface chemical investigation in Hungary. It has also to be mentioned that an earlier model of KRATOS ES 300 has been installed recently in the Institute of Isotopes of the H.A.S.

The KRATOS XSAM 800 instrument is equipped with a dual anode X-ray source, of Mg K_α ($E = 1253.6$ eV) and of Al K_α ($E = 1486.6$ eV) radiation and with a 127 mm mean radius 180° deflection double focussing hemispherical electrostatic analyser. The X-ray gun can be operated with power up to 15 kV × 30 mA (450 W). The maximum signal intensity is 10^6 imp $\cdot$ s^{-1}, the signal to background ratio is 30, and the resolution characterized by the full width at half maximum (FWHM) of the $3d_{5/2}$ peak of Ag, is 0.83 eV. A highly efficient pumping system enables to reach 2×10^{-8} mbar in the preparation chamber and 10^{-10} mbar in the analysis chamber. After the introduction of a new, non-degassing sample, analysis can be started in about 5 min. Samples can be heated in situ up to 900 K or cooled down to 120 K. Surface cleaning or depth profiling can be done by neutral gas (Ar, Ne, Xe, He, N_2) ion etching with energies up to 5 keV in static or rastering modes. Data acquisition and data processing (integration, derivation, background subtraction, peak synthesis, peak comparison and subtraction, etc.) may be performed simultaneously using the KRATOS DS300 data system run on a DEC LSI 11/23 computer backed with a RX02 Double Floppy Disk System.

The present paper gives a short summary of the results obtained during the last two years in the Department of Solid State Chemistry of the Research Laboratory for Inorganic Chemistry of the H.A.S. The following examples reveal the three main fields of our own scientific problems, concerning mainly the gas-solid interactions, where the solids are predominantly oxides; basic research performed in the frame of foreign cooperations, and surface investigations oriented towards industrial problems. Consequently, the examples to be shown will cover the following areas: gas-solid reactions, catalysts and catalysis, layer structures, glass and mineral surfaces, polymers and coals.

Gas-solid reactions

Studying the kinetics of TiO_2 (anatase)$=COCl_2$ reaction enhanced reactivity has been observed in some cases. XPS investigations clearly revealed the presence of small amount of potassium impurity on the surface (Fig. 1) responsible for the observed effect [6].

In the $TiO_2 + SiCl_4$ system, the SiO_2 deposited forms a separate phase on the TiO_2 surface [13, 18] (Fig. 2).

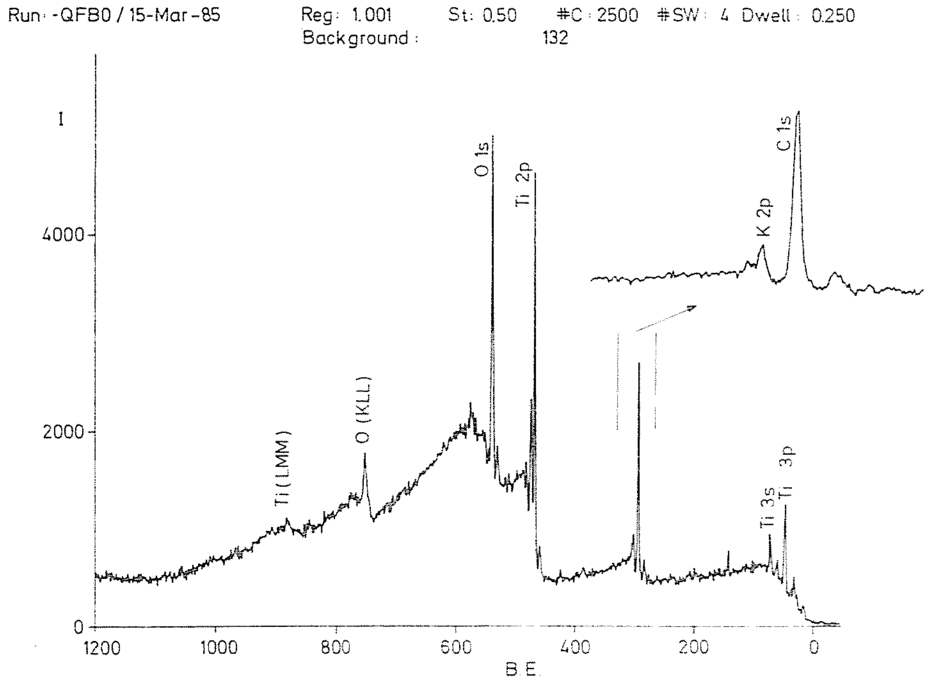


Fig. 1. Wide scan spectrum of an analytical grade TiO_2 (anatase) sample, showing the presence of a small amount of surface potassium contaminant (see insert with enlarged energy scale)

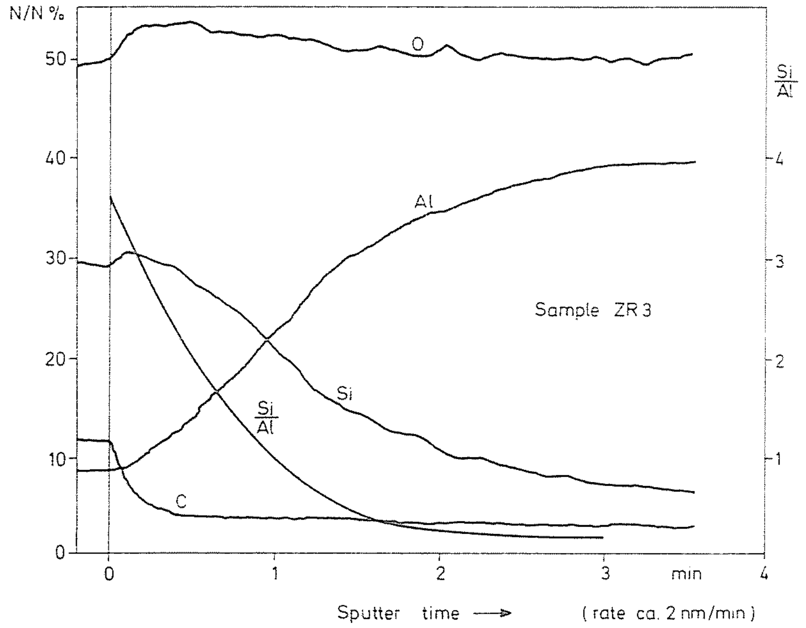
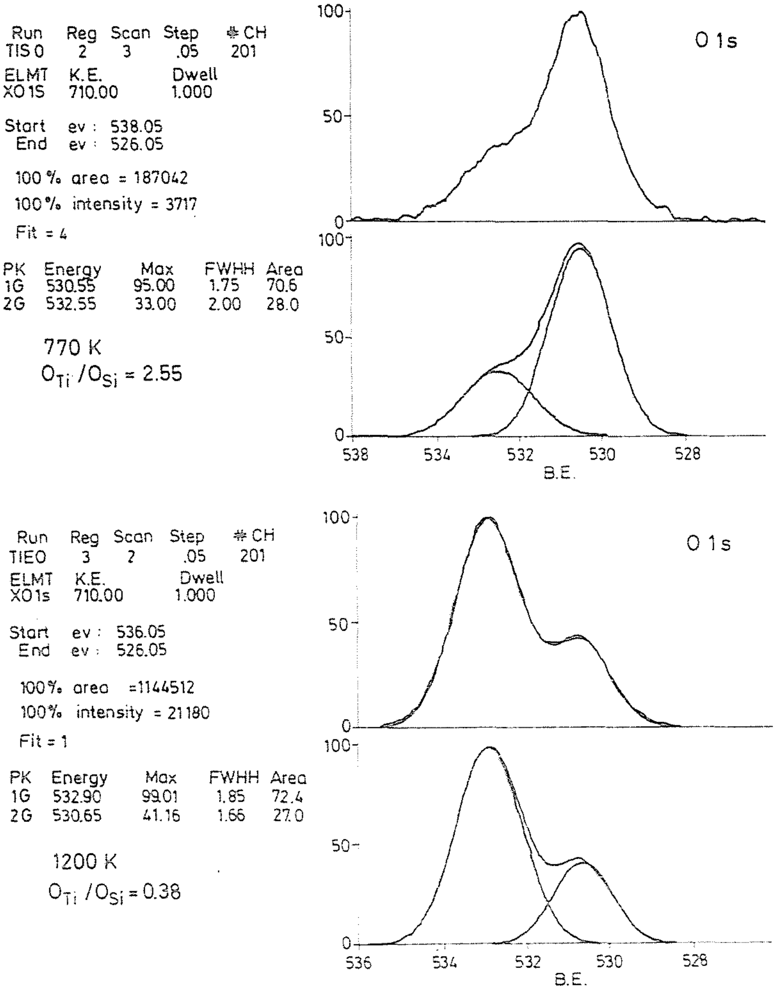


Fig. 2. Ar^+ ion depth profile of a silica-alumina surface phase, obtained by the reaction of $SiCl_4$ with α-Al_2O_3 (sapphyre) single crystal at 1200 K



```
Run    Reg  Scan  Step    # CH
TIS0    2    3     .05     201
ELMT   K.E.           Dwell
XO1S   710.00         1.000

Start   ev :  538.05
 End    ev :  526.05

100 % area = 187042
100 % intensity = 3717
Fit = 4

PK  Energy    Max     FWHH  Area
1G  530.55    95.00   1.75  70.6
2G  532.55    33.00   2.00  28.0
```

770 K

$O_{Ti}/O_{Si} = 2.55$

```
Run    Reg  Scan  Step    # CH
TIEO    3    2     .05     201
ELMT   K.E.           Dwell
XO1s   710.00         1.000

Start   ev :  536.05
 End    ev :  526.05

100% area  =1144512
100% intensity = 21180
Fit = 1

PK  Energy    Max     FWHH  Area
1G  532.90    99.01   1.85  72.4
2G  530.65    41.16   1.66  27.0
```

1200 K

$O_{Ti}/O_{Si} = 0.38$

Fig. 3. Characteristic changes in O 1s lines of TiO_2 reacted with $SiCl_4$ at different temperatures

For the $2V_2O_5+3CCl_4=4VOCl_3+3CO_2$ reaction the proposed mechanism involves formation of CO_2 via absorbed $COCl_2$, while surface vanadium atoms gains, chlorine atoms before the formation of $VOCl_3$. The surface vanadium species left are mainly in lower oxidation state in stationary stage of the reaction which has been proved by the observed chemical shift of the V $2p_{3/2}$ line [6–12].

In the $2Al_2O_3+3SiCl_4=4AlCl_3+3SiO_2$ reaction the SiO_2 deposited on the surface did not form a separate phase. This new surface phase could be of some ten atomic layers thick in the case of α-alumina [13] but the process stops at monolayer coverage in the case of γ-alumina [13–17].

Catalysts and catalysis

The valence states in the V_2O_5 and $PdO \neq = V_2O_5$ catalysts were studied in the $CO + \frac{1}{2}O_2$ reaction. The partial reduction and a steady state reoxidation of PdO and V_2O_5 was stated, e.g. the lattice oxygen atoms also take part in the catalytic cycle (Fig. 4). SiO_2 doped γ-Al_2O_3 and TiO_2 catalysts were produced by the reactions described above and these samples were very active in the cracking of hydrocarbons. The maximum catalytic activity was detected at $\Theta_{SiO_2} \approx 0.2$ coverage and it was connected with the change of the electronic structure of the surface which could be also described as a maximum curve versus the SiO_2 coverage [14, 20].

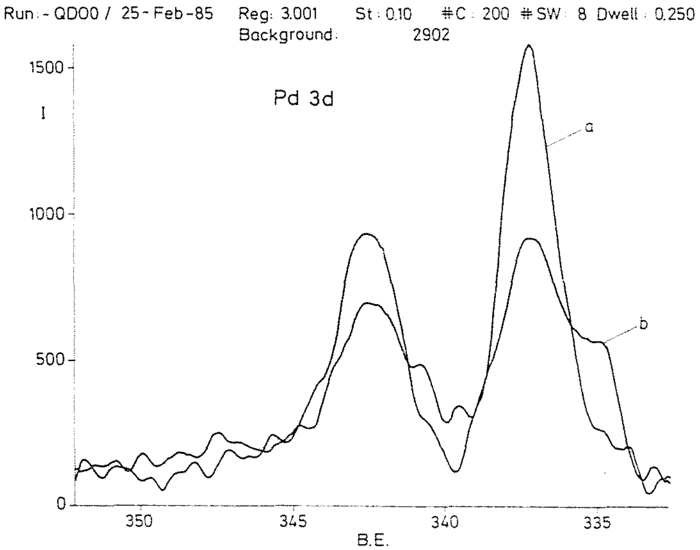


Fig. 4. The change of oxidation state of Pd during catalytic process: (a) oxidised state, (b) partly reduced state after exposure to CO

Layer structures

- Formation of SiO_2 layer on TiO_2 surface [18].
- Structure determination of the surface additives of TiO_2-based pigments [21].
- Depth profiling of oxide and nitride layers on Si semiconductor and Ti surfaces.
- Studies on metal contacts of Si solar cells: oxidation, diffusion, depth distribution changes by heat treatment [23].
- Studies on surface segregation and carbide formation of alloys and high-speed steel [24].

Glass surfaces

The surface enrichment and depletion of alkaline metals (Na) by water rinsing and chemical treatment [25] and the alteration of the surface composition by subsequent heat treatment [26, 37] were studied.

Mineral surfaces

Studying quartz sand, the surface enrichment of impurities and the concentration changes in the processing steps and during special chemical treatments were observed [29].

Polymers and coals

- Changes in composition and bonding, induced by soft X-rays or bombardment with Ar^+ or N_2^+ ions in a commercial poly-methyl-phenyl-cyanopropyl-siloxane fluid were examined [28–31] (Fig. 5).
- Characteristic surface segregation versus bulk composition was detected on silane-siloxane block copolymers suitable for manufacturing semipermeable membranes for selective gas-separation processes. Moreover, the surface composition could be altered in a controlled way by adequate solvents [32].
- Changes in surface composition and bonding on polyimides during heat treatment up to 1200 K was followed [33, 34].
- Contaminants in the insulating layers of cross-linked polyethylene cables, as well as at the metal-polymer interface were analysed.
- Complementary quantum chemical calculations showed that oxygen (always present in each sample) would facilitate the excitation of HOMO electrons and reduce the band gap [35, 38].
- Information on surface effects of various pretreatments of some Hungarian brown coals was obtained: changing in composition and bonding of the constituent elements was followed after exposure to UV-irradiation in air, after desulfurization by hydrogen-peroxyde or carbonization by heat treatment [36] (Fig. 6).

The above results demonstrate the possibilities of XPS technique in diverse fields of basic and applied surface investigations, and also represent the wide applicability of a third generation ESCA instrument.

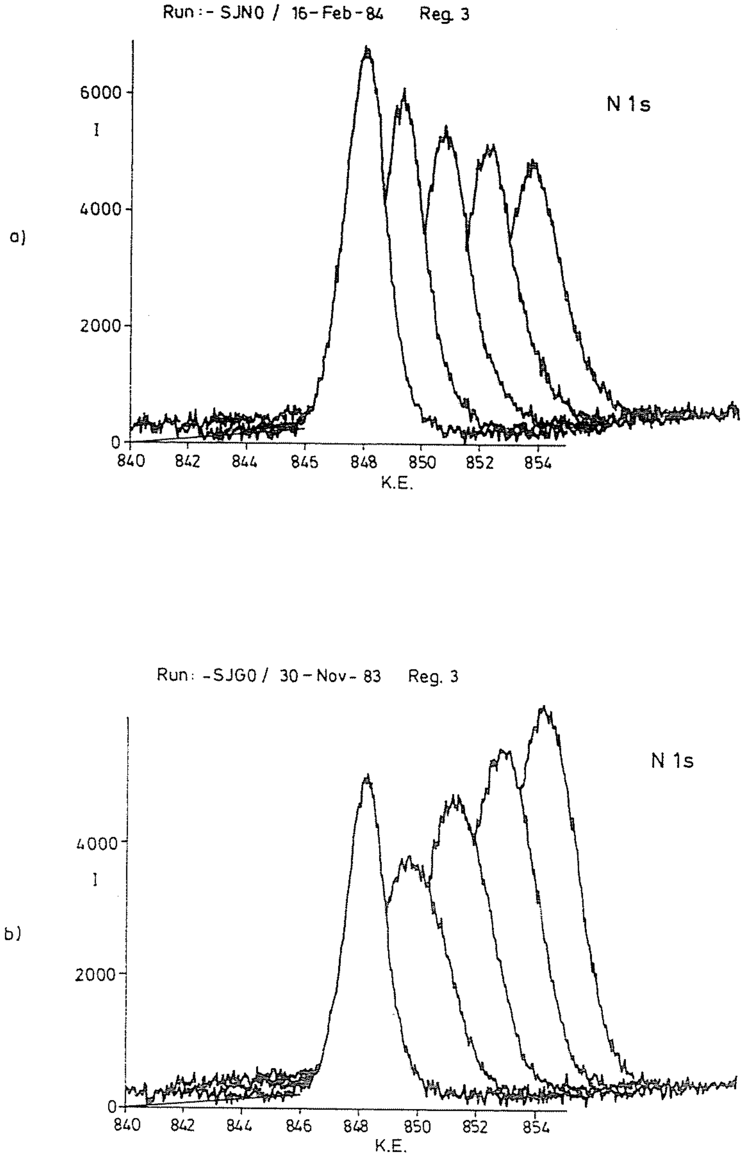


Fig. 5. Three-dimensional plot of the N 1s peak of the polymer exposed to X-ray irradiation (a) and bombardment by N_2^+ ions (b)

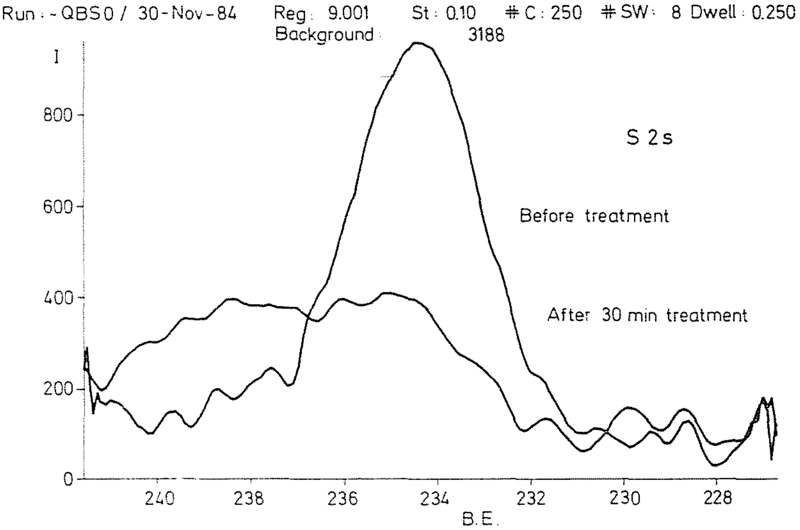


Fig. 6. Change in the S 2s peak of Kányás coal before and after treatment by H_2O_2

References

1. SIEGBAHN, K. Co.: ESCA Applied to Free Molecules. North-Holland Publ. Co. Amsterdam, 1969.
2. BAKER, A. D.–BETTERIDGE C.: Photoelectron Spectroscopy. Pergamon Press, Oxford–New York–Toronto–Sydney–Braunschweig, 1972.
3. BERÉNYI, D.: Az ESCA módszer alapjai és legújabb eredményei. A kémia újabb eredményei 35. Akadémiai Kiadó, 1977.
4. BERÉNYI D.: Fotoelektronspektroszkópia: UPS, XPS. A szilárdtestkutatás újabb eredményei, 5. Akadémiai Kiadó, 1979.
5. VARSÁNYI GY.–VESZPRÉMI T.–BERTÓTI I.: Fotoelektronspektroszkópia, BME Mérnöki Továbbképző Int. 1985.
6. MINK, GY.–BERTÓTI, I.–PAP, I. S.–MOHAI, M.–SZÉKELY, T.–TRAN MINH DUC: On the Effect of Surface Potassium upon the Reactivity of Titania. 3rd Joint Vacuum Conference (Hungarian–Austrian–Yugoslavian), Oct. 1985. Debrecen
7. MINK, G.–BERTÓTI, I.–PAP, I. S.–SZÉKELY, T.–BATTISTONI C.–KARMAZSIN E.: Thermochimica Acta *85*, 1985, 83.
8. MINK, G.–BERTÓTI, I.–BATTISTONI, C.–SZÉKELY, T.: React. Kinet. Catal. Lett. *27*, 39 1985.
9. MINK, G.–KARMAZSIN, E.–SZÉKELY, T.–BERTÓTI, I.: Kinetic study of the chlorination of V_2O_5 and TiO_2 with CCl_4 (Lyon, Laboratoire de Physico-Chimie Minerale I.B. Villeurbanne, 8, 09, 83. Société Chimique de France)
10. MINK, G.: On the kinetics and mechanism of the chlorination of vanadium and titanium oxides. (ZIAC Seminars, Berlin, Apr. 1983)
11. MINK, G.: On the reaction mechanism of the chlorination of V_2O_5 studied by TG, MS, ESCA and volumetric adsorption methods. (Research Center of CNR, Roma, Oct 1982)
12. MINK, G.–BERTÓTI, I.–PAP, I. S.–SZÉKELY, T.–BATTISTONI, C.–KARMAZSIN, E.: Thermochimica Acta *85*, 83 1985., Third European Symposium on Thermal Analysis and Calorimetry (Interlaken, Switzerland, Sept. 1984)

13. Székely, T.–Bertóti, I.–Mink, G.–Tóth, A.: Topochemische Betrachtung von Oberflachenreaktionen bei der Chlorierung von Oxyden und Mehrkomponentensystemen (III. Arbeitstagung der Arbeitsgemeinschaft Festkörperchemie. Dec. 1984. Bad Schandau)
14. Székely, T.–Bertóti, I.–Mink, G.–Till, F.–Réti, F.: Inorganic chemistry of some modifications of the surfaces of oxide catalysts (MTA-USA NSF "Workshop for Surface Science and Catalysts" July 1984)
15. Pödör, B.–Bertóti, I.–Székely, T.–Battistoni, C.: Investigations on the chlorination reactions of metal oxides (4th Seminar of Soc. Countries on Electron Spectroscopy, Moscow, May 1982)
16. Bertóti, I.: Kinetic studies on chlorination reactions by TG, MS, SEM and ESCA methods (ZIAC Seminars, Berlin, Apr. 1983)
17. Bertóti, I.: On the kinetics of the chlorination of metal oxides (Research Center of CNR, Roma, Okt. 1982)
18. Bertóti, I.–Mink, G.–Székely, T.–Ebel, H.–Zuba, G.: XPS Studies on the Chlorination of TiO_2 by $SiCl_4$. 5th SESSC (Seminar on Electron Spectroscopy of Socialist Countries) Dresden, Aug. 1984.
19. Mink, G.–Bertóti, I.–Bessenyei, G.–Székely, T.: Influence of the form of V_2O_5 on the surface and catalytic behaviour. MTA-USA NSF Workshop.
20. Varsányi, Gy.–Bertóti, I.–Mink, G.–Réti, F.–Révész, M.: SiO_2-vel adalékolt γ-Al_2O_3 katalitikus tulajdonságai. Visegrád, Apr. 1985.
21. Mink, G.–Bertóti, I.–Réti, F.–Mohai, M.: TiO_2-alapú pigmentek minősítése fizikai, kémiai és felelületanalitikai (XPS) módszerekkel. Technical Report July 1984.
22. Sobczak, E.-Wokulski, E.–Bertóti, I.–Zuba, G.: XPS Studies of TiN_x Real Surface. 5th SESSC.
23. Bertóti, I.–Tóth, A.–Mohai, M.: Si-napelemeken kialakított fémkontaktusok XPS vizsgálata. Technical Report Aug. 1984.
24. Menyhárd, M.–Gergely, G.–Sulyok, A.–Bertóti, I.: Electron Spectroscopy Study of Carbides in AISI M2 High Speed Steel. 5th SESSC.
25. Bertóti, I.–Tóth, A.–Révész, M.–Mohai, M.–Réti, F.: Mállott üvegfelületek ESCA vizsgálata. Technical Report Sept. 1984.
26. Bertóti, I.–Révész, M.–Mohai, M.: Termikus megmunkálással kialakított gyógyszerüvegek ESCA vizsgálata. Technical Report Oct. 1984.
27. Bertóti, I.–Szépvölgyi, J.–Mohai, M.: Studies on Quartz Sand Beneficiation Technology. UNDP Technical Report No. 1. Dec. 1984.
28. Székely, T.–Till, F.–Tóth, A.–Bertóti, I.–Mohai, M.: Analiz i issledovanie radiacionnokhimicheskich prevrashcheniy poli-metil-fenil-cianopropil-siloksana metodom RFES. 9. Mezhdunarodniy mikrosimpozium po polikondensacii, Budapest, Sept. 1983.
29. Székely, T.–Tóth, A.–Bertóti, I.–Mohai, M.: Study on the Effect of Ionized Inert Gas Bombardment of Polysiloxane Fluids with the Aid of XPS. VII. Int. Symp. on Organosilicon Chem. 1984. Kyoto, p. 103.
30. Tóth, A.–Bertóti, I.–Székely, T.–Mohai, M.: XPS Study on Poly-Methyl-Phenyl-Cyanopropyl-Siloxane Bombarded by Ionized Inert Gases. 5th SESSC.
31. Tóth, A.–Bertóti, I.–Székely, T.–Mohai, M.: Surface and Interface Analysis 7, 282 (1985).
32. Tóth, A.–Gladkova, N. K.–Bertóti, I.–Durgarjan, S. G.–Székely, T.–Filippova, V. G.: J. of Polym. Science, Pol. Chem. Ed. (to be published)
33. Sazanov, J. N.–Székely, T.–Antonova, T. A.–Shchukarev, A. B.–Tóth, A.–Bertóti, I.–Gribanov, A. V.: Termokhimicheskie reakcii poliimidov (to be published)
34. Tóth, A.–Bertóti, I.–Székely, T.–Antonova, T. A.–Sazanov, J. N.: XPS Study on Thermal Degradation of Poly-N,N'(4,4'-Diphenylether)-Pyromellitimide. European Conference on Application of Surface and Interface Analysis, Oct. 1985. Veldhoven, The Netherlands (In press)

35. SZÉKELY, T.–BERTÓTI, I.–TÓTH, A.–RÉVÉSZ, M.–RODER, ZS.–PAP, I. S.: Térhálós polietilén szigetelésű kábelek vizsgálata, Technical Report 1985.
36. TÓTH, A.–BERTÓTI, I.–SZÉKELY, T.–RÉVÉSZ, M.–SZÉPVÖLGYI, J.–MOHAI, M.: XPS Study on Some Hungarian Brown Coal Samples, Research Account for the UNIDO, 1984.
37. BERTÓTI, I.– MOHAI, M.–RÉVÉSZ, M.–ALEXANDER, G.: Surface composition of glasses: modifications induced by chemical treatments. Third Joint Vacuum Conference (Hungarian–Austrian–Yugoslavian) Oct. 1985. Debrecen (In press)
38. RÉVÉSZ, M.: Oxigén szennyezések hatása polietilének ionizációs potenciáljára és elektrongerjesztéseire. XXVIII. Magyar Színképelemző Vándorgyűlés June 1985. Eger

Imre BERTÓTI
György MINK
András TÓTH
Márta RÉVÉSZ
Miklós MOHAI
Tamás SZÉKELY
H-1502 Budapest POB. 132