Thermogravimetry (TG) coupled to soft single photon ionisation quadrupole mass spectrometry for analysis of the release of organic molecules during thermal treatment of organic material: Thermal decomposition of polyethylene and polyvinylchloride

M.Saraji-Bozorgzad[1,2], M.Sklorz[1,2], R.Geißler[1,2], T.Streibel[1,2], E.Kaisersberger[3], T.Denner[3], R.Zimmermann[1,2,4]

(1) GSF-National Research Center for Environment and Health, Institute for Ecological Chemistry, D-85764 Neuherberg, Germany (ralf.zimmermann@gsf.de)
(2) Universität Augsburg, Institut für Physik, D-86159 Augsburg, Germany
(3) Netzsch-Gerätebau GmbH, D-95100 Selb, Germany
(4) BIfA GmbH, D-86167 Augsburg, Germany

Abstract:
A newly developed prototype of a thermogravimetry - single photon ionisation quadrupole mass spectrometer coupling (TG-SPI-QMS) was applied to study the molecular fingerprint in the evolved gases from thermal composition of two common plastics (polyethylene (PE) and polyvinylchloride (PVC)). While the decomposition of PE takes place in a one step process (main weight-loss: 480-510 °C) under emission of the homologous series of alkenes, PVC decomposes in two step mechanism. Firstly hydrogenchloride (HCl) is eliminated in a hydrodechlorination reaction (1st weight-loss step: 285-305 °C). This is accompanied by the emission of the carbon skeletons of small aromatics (predominately benzene and naphthalene). In the second step (2nd weight-loss step: 490-510 °C), the residual cross-linked polyolefin moieties decompose under release of heavily alkylated aromatics, including larger PAH. Chlorinated aromatics are formed only in trace levels. The potential of hyphenating thermogravimetry and soft photo ionisation mass spectrometry (EBEL-SPI-MS) for fundamental and applied research and material analysis has been demonstrated.

Introduction:
In thermogravimetry (TG) the course of the weight loss of a sample due to pyrolysis and vaporisation processes during a thermal protocol is recorded. For many industrial applications the informations obtained from the TG curve (thermogram: sample weight vs. temperature curve) or the differential thermal analysis curve (DTG, differential thermogram: first derivative of sample weight vs. temperature curve) are used for e.g. quality control or applied material research. For more advanced applications, however, a chemical analysis of the evolved gases is required. This can be done either by coupling of TG to a sequentially working analytical device such as gas chromatography (with or without mass spectrometric detector, TG-GC(-MS))[1] or by coupling of on-line real-time analytical technology. Examples for the latter are Fourier-Transform infrared spectrometry for analysis of organic main products and mass spectrometry (MS)[2]. The MS method commonly used in conjunction with TG is quadrupole MS with electron impact ionisation. The coupling between the TG oven and the mass spectrometer is realised either via a transfer capillary or a skimmed supersonic expansion. Although MS is a very powerful analytical technique for molecular analysis, the currently available TA-MS systems have problems in showing the composition of the organic trace species in the evolved gases. This is mainly due to the fact that electron impact ionisation with 70 eV electrons causes a large extent of fragmentation of organics. First thermal desorption studies, pyrolysis studies[3,4] as well as TG studies using laser based soft ionisation mass spectrometry as detector[5] revealed that highly valuable molecular information on the thermal decomposition processes can be achieved. In this contribution, a newly developed prototype of a TG-single photon ionisation quadrupole mass spectrometer coupling (TG-SPI-QMS) is presented. Exemplarily, data on TG runs with the polymers polyethylene (PE) and polyvinylchloride (PVC) are shown. An electron beam pumped rare gas excimer VUV-lamp (EBEL) is used for the soft photo ionisation process[6-8].

Experimental:
The working principles of the EBEL[9] and the EBEL-QMS system were described previously in the literature[7,8]. Briefly, a homebuilt EBEL-VUV light source was used for single photon ionisation in a QMS system (QMS 200, 6-mm rod system, Balzers-Pfeiffer, Switzerland). The main innovation of the novel EBEL-VUV light source is a

0.7×0.7 mm² ceramic silicon nitride (SiNx) foil of only 300 nm thickness that separates the rare gas volume (p > 1 bar) from a vacuum chamber containing an electron gun (EG). The EG generates a 13-keV electron beam which is shot into the rare gas through the SiNx foil with low-energy loss. The energetic electrons excite and ionise the rare gas atoms. In successive processes, excited diatomic rare gas molecules (excimers) are formed. Upon the radiative decay of these excimers, VUV-radiation is emitted. As a result of the high gas pressure, the excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The rare gas volume was filled with Ar (emission maximum: 126 nm, 9.8 eV centre photon energy) for the here presented study. The EBEL SPI-QMS exhibit detection limits in the 50 ppb range for a scan rate of 1 m/z s⁻¹. Note that future TA-EBEL-SPI-MS systems will be equipped with more intense EBEL sources as well as with more powerful mass analyzers (larger quadrupole system with 8 mm rod system or time-of-flight mass spectrometers) and thus will exhibit further decreased detection limits. For the here presented experiments on PVC and PE, the gas inlet of the QMS was coupled via a heated transfer line to the TG system (Netzsch, Selb, Germany). A special adapter and transfer line (250°C) were developed for the TG-system to avoid memory effects of released higher boiling compounds. The experiments were performed under nitrogen atmosphere and at a heating rate of 40 °C/min. A sketch of the setup of the device is shown in Figure 1. A commercial system based on the here presented prototype is currently under development in cooperation with the company Netzsch-Gerätebau GmbH, Selb, Germany.
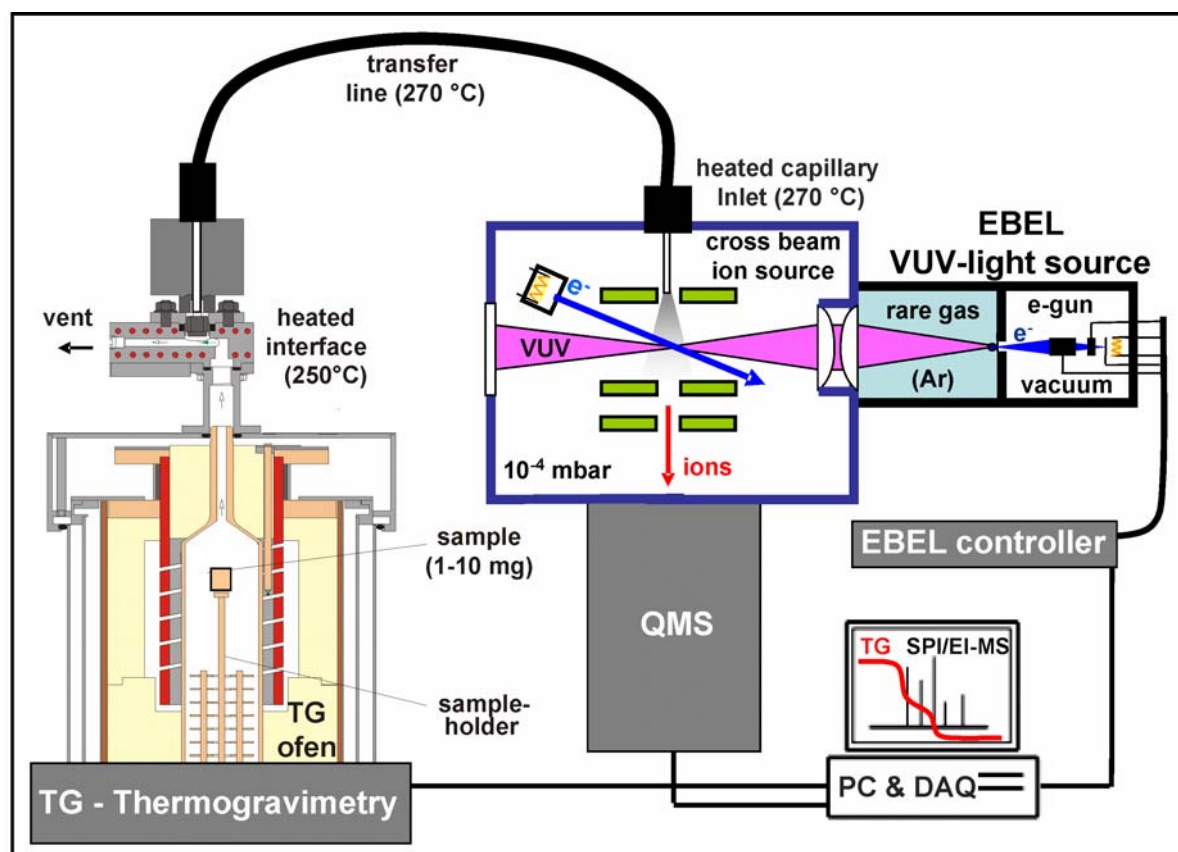

Figure 1: Schematic representation of the TG-EBEL-SPI-QMS prototype.

Results and Discussion

In first experiments the novel TG-EBEL-SPI-QMS device was applied to analyse the thermal decomposition of two common plastics, namely of polyethylene (PE) and polyvinylchloride (PVC). It is known from literature that the main products of PE pyrolysis are unsaturated hydrocarbons (alkenes, polyenes) as well as some alkanes, while the amount of aromatic products is low[10].
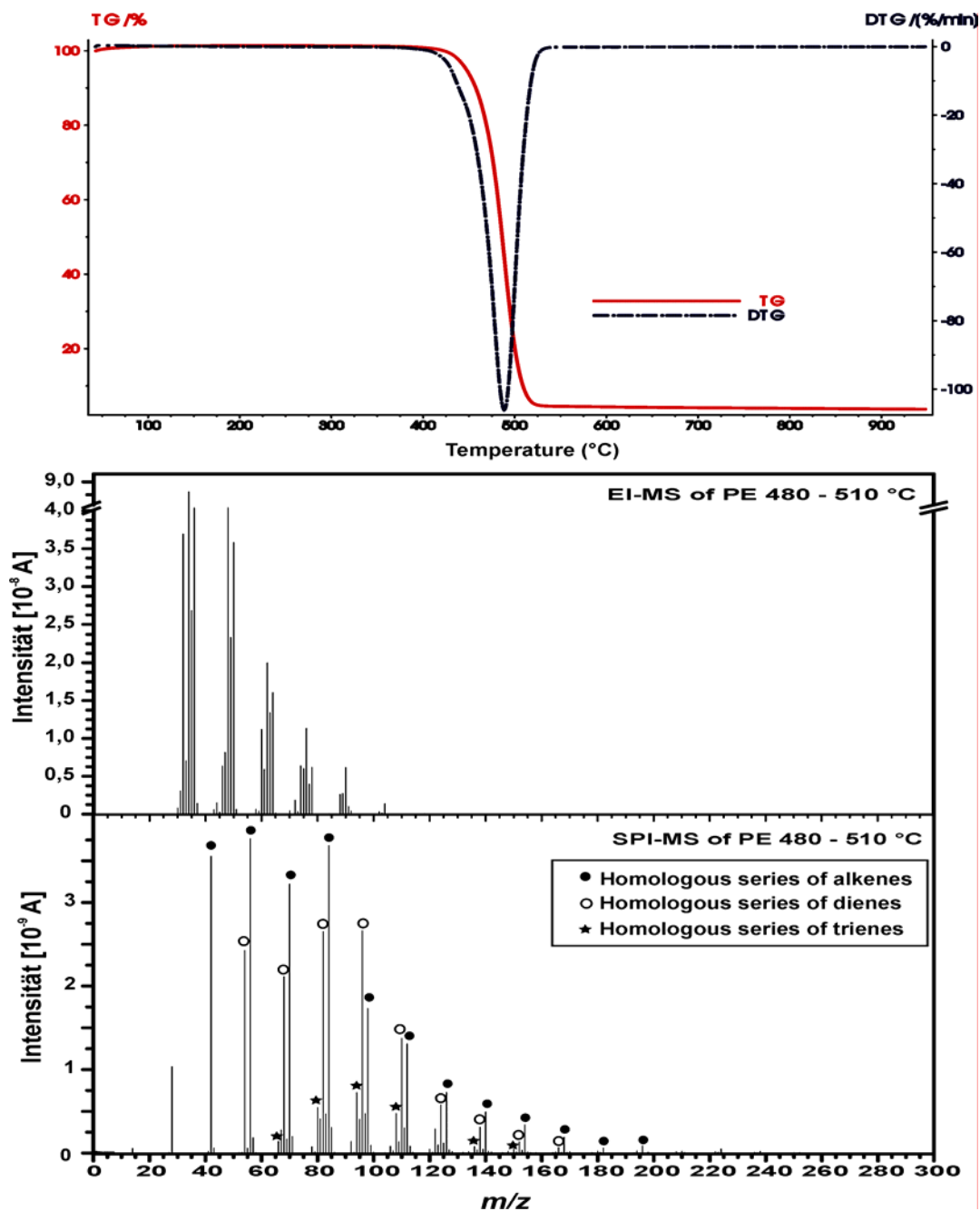
Figure 2: Thermogravimetry-single photo ionisation quadrupole mass spectrometry (TG-SPI-QMS with EBEL) of polyethylene (PE): Top) TG and DTG curves; Middle) Electron impact mass spectrum (EI, 70 eV); Bottom) SPI mass spectrum recorded during the maximal decomposition rate.

Figure 2 shows the TG/DTG curves of PE (upper panel) as well as two mass spectra obtained from the evolved gases at 480-510 °C, using either conventional EI ionisation (middle panel) or the EBEL-SPI photo ionisation (lower panel). Note that the used lamp for SPI (Ar-excimer, 9.8 eV) does not address the smaller alkanes. The EI mass spectrum is dominated by fragments. From the EI mass spectrum it can only be stated that the content of aromatics is rather low in comparison to the aliphatic pyrolysis products. In contrast, the soft EBEL-SPI mass spectrum reveals clearly the homologous series of alkenes, dienes as well as trienes up to C_{14}.
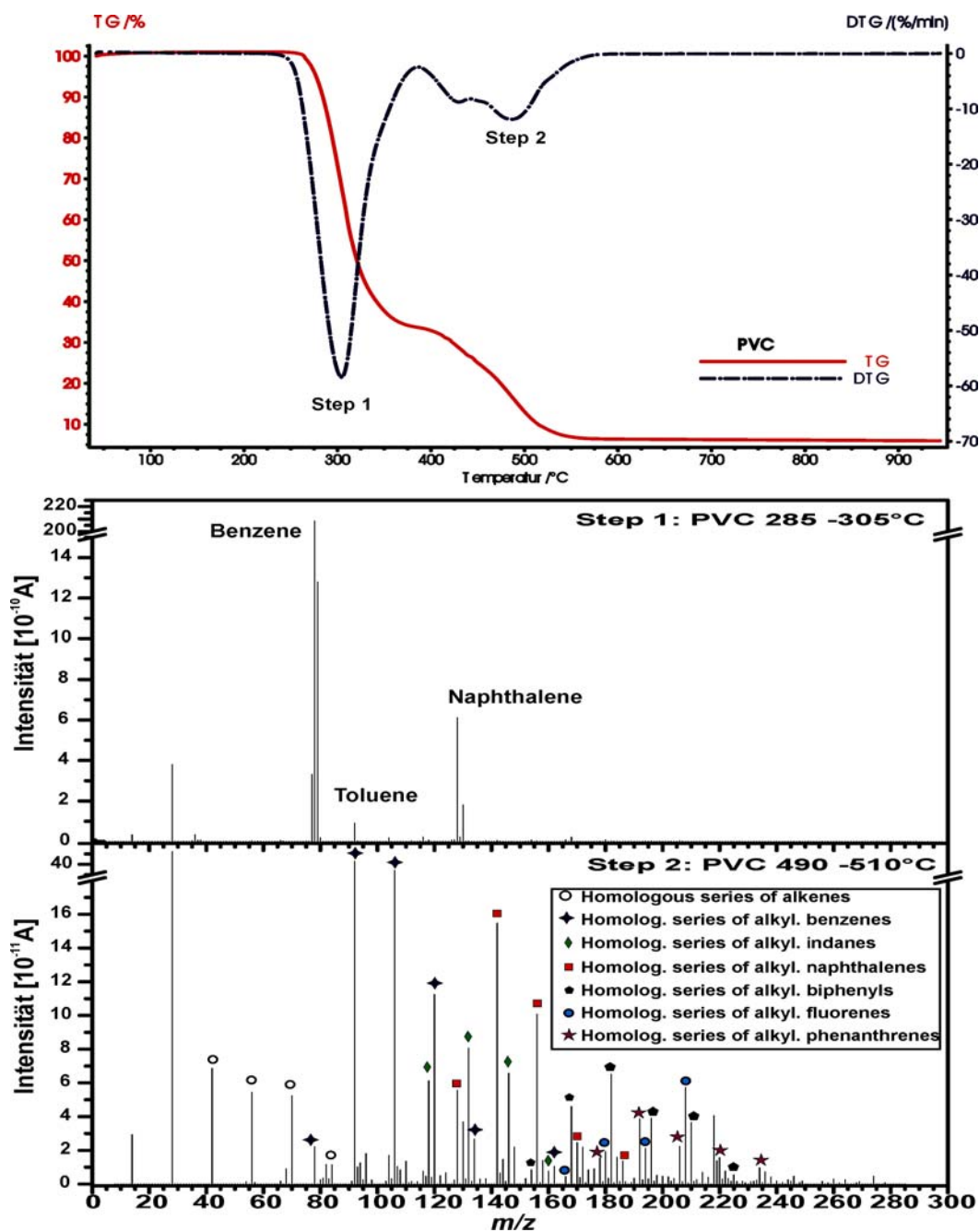
Figure 3: Thermogravimetry-single photo ionisation quadrupol mass spectrometry (TG-SPI-QMS with EBEL) of polyvinylchloride (PVC): Top) TG and DTG curves; Middle) SPI mass spectrum of the first decomposition step; Bottom) SPI mass spectrum of the second decomposition step.

With a further improved heated inlet, it should be possible to see even higher mass PE pyrolysis products. Although the SPI cross-section of aromatics is slightly higher (~ factor of 2) in comparison to those of alkenes, only a very minor signal of benzene is detectable at 78 m/z. As the technology allows a real-time on-line analysis, the chain length distribution of the evolved organic species can be monitored as function of the temperature. This motivates further studies on the mechanisms of thermal polymer degradation. The thermal decomposition of

polyvinylchloride (PVC) is much more complicated than the one of PE[10]. Briefly, PVC decomposes in a two-step mechanism. The first step is due to a hydrodechlorination process (HDC), where HCl is eliminated (in the TG-EI-QMS experiment strong HCl signals are visible) leaving a polyolefinic structure as residue[10,11]. From the polyolefin moieties efficiently benzene is formed. Different mechanisms have been proposed for the HDC and benzene formation. For example, a radical chain mechanism for the HDC, involving Diels-Alder-type reactions for formation of the benzene moieties was proposed by Bockhorn et al.[10]. The residual polyolefin structure is believed to undergo cross-linking reactions. In the further course of the decomposition process the cross-linked polyolefin structures release a very complex mixture of monocyclic as well as condensed substituted aromatic compounds. The final residue then represents a char-like, refractory material. In Figure 3, the TG and DTG curves of PVC (upper panel), as well as TG-EBEL-SPI-QMS mass spectra of the first (middle panel) and second (lower panel) weight loss step are shown. The TG and DTG curves clearly show the well known two step decomposition behaviour (steps at ~ 275 °C and at ~375 °C) of PVC. The soft ionisation mass spectrum recorded at the maximal weight loss rate of the first step (285-305 °C) depicts predominantly benzene and naphthalene in accordance with the literature. This, however, can also be seen by EI mass spectrometry, due to the relative fragmentation-resistance of aromatic structures. The picture changes if the second weight loss maximum at 490-510 °C is considered. During the decomposition of the cross-linked polyolefin structure a complex pattern of aromatic carbon skeletons evolves with various alkyl substitutions. In particular homologous series based on benzene, indane, naphthalene, biphenyl, fluorene and phenanthrene are detectable. In most cases, the C_1-substituted congener is the most abundant one (monomethyl derivatives). According to the theory, the structure of the cross-linked polyolefin determines the profile of the substitutions. As the evolution of the substitution profile is now dynamically detectable by SPI-MS, a re-evaluation of the current of the thermolysis of PVC might is of interest. Note, that chlorinated benzenes (PCBz) have not been detected under the current experimental TG-SPI-QMS conditions. This is in contrast to the results of preceding flash-pyrolysis experiments with laser based EBEL-SPI-TOFMS detection[4]. Here strong PCBz signals as well as signals of chlorinated phenols (PCPh, in experiments under oxygen containing atmosphere) were detected[4], which suggest also the formation of chlorinated ultra trace components such as polychlorinated dibenzo-p-dioxins und furans (PCDD/F) and polychlorinated biphenyls (PCB). The reason for the formation of chlorinated aromatics in case of rapid heating of the PVC sample to temperatures above 600 °C (pyrolysis) might be the "override" of the above described hydrodechlorination process which takes place at lower temperatures during a slowly heating of the sample and removes the majority of the chlorine as HCl. The flash-pyrolytic breakdown of PVC at high temperatures in contrary takes place in the presence of the original chlorine content.

Conclusion:
The potential of hyphenating thermogravimetry and soft photo ionisation mass spectrometry (EBEL-SPI-MS) for fundamental and applied research and material analysis has been demonstrated. Exemplary results on the application in polymer science have been presented. The planned commercialisation of the TG-EBEL-SPI-MS system will make the technology available for a broader community. Future TG-EBEL-SPI-MS systems will be based on TOF mass spectrometers for more sensitivity, speed and mass resolution.

References
(1) Chiu, J. *Analytical Chemistry* 1968, *40*, 1516 - 1520.
(2) Raemaekers, K. G. H.; Bart, J. C. J. *Thermochimica Acta* 1997, *295*, 1-58.
(3) Cao, L.; Mühlberger, F.; Adam, T.; Streibel, T.; Wang, H. Z.; Kettrup, A.; Zimmermann, R. *Analytical Chemistry* 2003, *75*, 5639-5645.
(4) Adam, T.; Streibel, T.; Mitschke, S.; Mühlberger, F.; Cao, L.; Baker, R. R.; Zimmermann, R. *Journal of Analytical and Applied Pyrolysis* 2005, *74*, 545-464.
(5) Zoller, D. L.; Murray, V. J. *Energy & Fuels* 1999, *13*, 1097-1104.
(6) Zimmermann, R.; Mühlberger, F.; Ulrich, A.; Wieser, J. *Nachr. Chem.* 2007, *55*, 425-429.
(7) Mühlberger, F.; Streibel, T.; Wieser, J.; Ulrich, A.; Zimmermann , R. *Analytical Chemistry* 2005, *77*, 7408-7414.
(8) Mühlberger, F.; Wieser, J.; Morozov, A.; Ulrich, A.; Zimmermann , R. *Analytical Chemistry* 2005, *77*, 2218-2226.
(9) Wieser, J.; Murnick, D. E.; Ulrich, A.; Huggins, H. A.; Liddle, A.; Brown, W. L. *Review of Scientific Instruments* 1997, *68*, 1360-1364.
(10) Bockhorn, H.; Hornung, A.; Hornung, U. *Journal of Analytical and Applied Pyrolysis* 1999, *50*, 77-101.
(11) Anthony, G. M. *Polymer Degradation and Stability* 1999, *64*, 353-357.