

THE DISCOVERY OF THE EXCITATION OF LIQUID BIPHENYL AND PHENANTHRENE FLUORESCENCE BY FAST ELECTRONS; LAUDATIO ON THE INAUGURATION OF THE GERMAN SOCIETY FOR LIQUID SCINTILLATION SPECTROMETRY (DGFS)

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ABSTRACT. In 1949 Herforth and Kallmann published a paper on the first measurements of liquid organic compounds fluorescence after excitation by nuclear radiation, containing the results of L Herforth's thesis. Given that LSC 2001 took place in Germany and founded at that meeting the German Society for Liquid Scintillation Spectrometry (DGFS) elected L Herforth as a honorary member LSC 2001 became an occasion to remember the original works. With the honorary membership, the important contribution of L Herforth and H Kallmann to the development of liquid scintillation for its application in environmental monitoring, radiation protection, bioscience, and medicine has been appreciated.

INTRODUCTION

A considerable amount of radioactivity measurements are done using organic scintillators. Periodical conferences are devoted to these techniques; in nuclear medicine this type of measurement is one of the most important. In addition, organic scintillators are used for the measurement of very large items like trucks and waste containers and for the measurement of extremely weak radiation in nuclear dating and neutrino research. Until now, the papers on the excitation of fluorescence of liquid biphenyl and phenanthrene by fast electrons published by Lieselott Herforth and Hartmut Kallmann (Herforth and Kallmann 1949) have not been referenced at an international LSC meeting. These papers contain results of her thesis including the measurement of the fluorescent yield of molten biphenyl and phenanthrene.

DEVELOPMENT OF SCINTILLATION COUNTERS AT THE KAISER WILHELM INSTITUTE FOR PHYSICAL CHEMISTRY, BERLIN-DAHLEM

Inorganic scintillators, e.g. barium platinum cyanide (II) have been well known as substances for the detection of radiation since the beginning of the 20th century e.g. by observing the alpha particles through a magnifying glass (Elster and Geitel 1903). The discovery of photomultiplier tubes enabled the measurement of scintillations with a lower photon yield. Hartmut Kallmann, a student of Max Planck and a former assistant of Fritz Haber, was engaged in neutron photography when he started to register the scintillation process by a counting equipment instead of human eyes. After World War II, he continued his work at the institute together with his Ph.D students Immanuel Broser and Lieselott Herforth who conducted the experimental work. Both have been graduated on counting devices under the auspices of Hans Geiger.

The first investigations with ZnS (Cu) and CdS were continued with organic compounds mainly by Herforth in her thesis (Herforth 1948). The results of the work were published in a number of articles (Broser and Kallmann 1947a, 1947b, 1948; Broser et al. 1948; Herforth and Kallmann 1949; Herforth 1950) and contained the first results on the measurements with naphthalene. The discovery of organic compounds' scintillation is described in several reviews (Spruch 1978; Stolz and Herforth 1988, Broser 1998, Niese 1999, 2001a, 2001b).

SYSTEMATIC INVESTIGATIONS ON THE SCINTILLATION OF ORGANIC COMPOUNDS

Liselott Herforth (Herforth 1948) was Kallmann's doctoral candidate. She used naphthalene (Schering Company) in her first investigations. She realized that the substance gave good fluorescent yields

(especially after recrystallization), while results with moth powder and mothballs from other companies varied with the purity of the material. Recrystallization with methanol and glycol gave high light yields, while the use of chlorinated hydrocarbons resulted in lower yields because of the effect now referred to as chemical quenching.

The lower photon yield observed after absorption of alpha particles in comparison to electrons (Broser et al. 1948) was explained by self-quenching due to the high ionization density. Therefore, aromatic compounds are more suitable for the detection of electrons compared to inorganic compounds. They also observed a different decay time behavior of the emitted photons between alpha and beta particles—an effect that is applied in modern liquid scintillation counters for alpha/beta pulse shape discrimination.

Herforth found that the photon yield of sublimated scintillators decreases with increasing temperature and maintains a lower value after melting. From the energy spectra she concluded that the absorbed energy was transferred to the excitation of the low bound electrons from the double bonds in the aromatic hydrocarbons. Her calculation showed that in phenanthrene 10% of the absorbed energy was emitted as photons with a wavelength of 450 nm. She concluded that, unlike inorganic crystals, the organic molecules do not influence each other. Her investigations on spectra, photon yields, and decay times of a number of condensed aromatic hydrocarbons showed their dependency on chemical structure, impurities, and type of radiation (Herforth 1950).

THE FIRST MEASUREMENTS OF THE SCINTILLATION OF LIQUID ORGANIC COMPOUNDS

In their paper Herforth and Kallmann (1949) presented the results of the measurement of the fluorescent yield of molten biphenyl and phenanthrene. The fact that the yield of molten aromates was one order of magnitude smaller than in the solid state was explained by self-quenching due to high scintillator concentrations. As known from the measurement of the optical fluorescence excitation by ultraviolet light (Herforth 1948), the excitation energy was transferred into kinetic energy of the molecules (Herforth and Kallmann 1949).

The dependency of the photon yield on the conditions of crystallization was explained by the structure of the solid phase. Between the crystals interactions take place, yielding a special type of quenching. The stronger quenching of identical than foreign molecules in solutions was explained by a special resonance interaction causing a strong attraction of the molecules and the approximation of the corresponding potentials curves. From the similarity of the light spectra caused both by the excitation of electrons and ultraviolet light she concluded that the quenching mechanism of the fluorescent light is similar. Thus, concentration quenching resulting in transformation of excitation energy of molecules into kinetic energy explains the low photon yield of pure molten aromatics and gives the direction of photon yield enhancement in liquid scintillation counting (LSC). The lower quenching in solid materials demonstrates that the molecules in this state only seldom come close together by thermal oscillation to be able to convert the electronic energy of the molecules into kinetic energy.

At the end of 1948, H Kallmann moved to the United States where he continued to research the energy transfer in the scintillation process in organic liquids (Kallmann and Furst 1950). Lieslott Herforth continued her career at the Institute of Medicine and Biology in Berlin-Buch where she applied the fluorescence of organic compounds to the detection of carcinogenic substances.

However, the most important further contributions in the development and application of organic scintillators were done in the USA in the 1950s and 1960s as described comprehensively in paper 01/01 (see also Rheinberger 2001).

CURRICULUM VITAE OF LISELOTT HERFORTH

Lieselott Herforth, born September 13, 1916 in Altenburg in Thuringia, studied physics at the Technical University in Berlin and completed a diploma work on counting tubes under the auspices of

Hans Geiger. She defended her thesis under the supervision of H Kallmann on September 13, 1948 on the work described in this paper. Between 1949 and 1954, she worked at the Institute of Medicine and Biology of the German Academy of Sciences in Berlin–Buch and became a lecturer of radiation physics at the Faculty of Mathematics and Natural Sciences of the University of Leipzig.

Between 1955 and 1960 she was responsible for training in the field of isotope application at the Institute for Applied Radioactivity of the German Academy of Sciences in Leipzig. Her textbook on experimental training of applied radioactivity (Herforth and Koch 1959) has been reprinted many times and translated into various languages.

In 1960 she became Professor and Head of the Institute for Applied Radioactivity at the Technical University in Dresden where in 1965 she became the first female university rector in Germany. She was member of the Society of Physics, Chemistry and Biophysics, and served on the scientific boards of the journals *Radioanalytical and Radiochemical Letters*, *Experimentelle Technik der Physik*, and *Isotopenpraxis*.

In 1969 she was elected a member of the German Academy of Science, the People's Chamber, and the Privy Council of the GDR, her work focusing on organizing a close contact between education, science, and industry.

After her retirement in 1976, she was engaged in a number of councils, scientific societies, and at the Academy of Science she was involved in a broad field of nuclear techniques application and radiation protection.

She is a member of the Leibniz Society of Berlin and was elected as an honorary member of the recently founded Deutsche Gesellschaft für Flüssigszintillations-spektrometrie (DGFS).

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