

**NEW POSSIBILITIES IN PULSED
RADIATION PHYSICS AND
CHEMISTRY WITH USE OF
DENSE PLASMA FOCUS DEVICE**

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Contents

- **Introduction**
- **Apparatus**
- **Characteristic scales**
- **Chemical reactions at short-pulse radiation - factors that influence their kinetics**
- **Experiments**
- **Conclusions**

Introduction

Classical “pulsed radiation chemistry” usually deals with relatively “weak” beams of radiation (low power flux density) and operates by terms of “doses” (D); the same is true for the physics of radiation interaction with matter and for radiation biology

In all these cases only the absolute number of ionizing particles or photons interacting with the object is important

The primary assumption in all these models is that each fast particle or X-ray photon interacts with the object *independently* from the others

On the contrary, in principal pulsed radiation physics and chemistry should operate with “instantaneous” flashes of radiation; however, it is physically impossible to produce momentary pulses

As a result, we must take into account “dose power”
– $P = D/\Delta t$ (where Δt is a duration of a pulse) as well

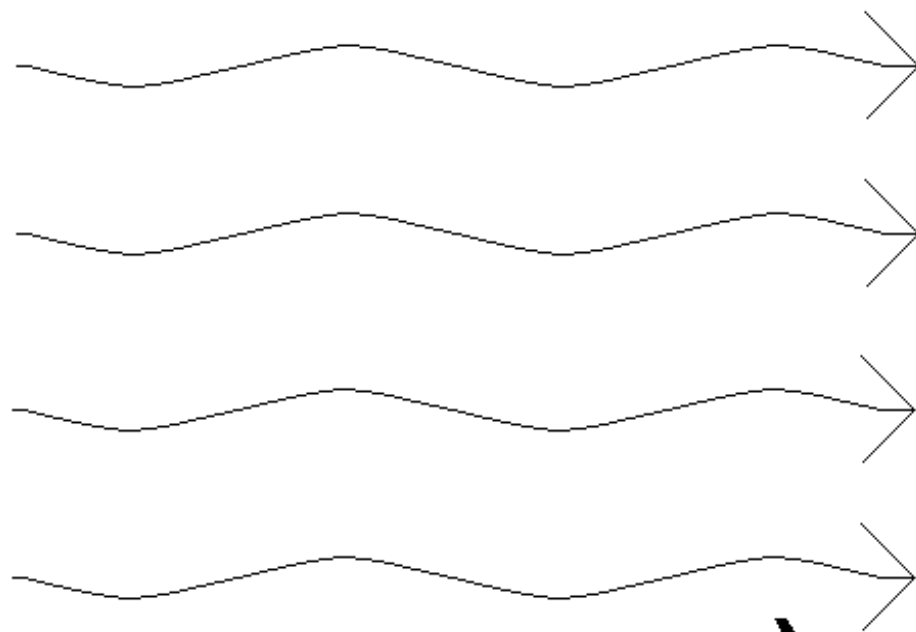
(Classical term “dose rate” is not convenient in this case because at the bell-like shape of a pulse during its rise the dose rate will be positive whereas during the second half of the pulse it will be negative)

Thus in the fields of pulsed radiation physics and flash radiation chemistry the **interaction time** of ionizing radiation beams with objects (the beam pulse duration) must be *short compared with the duration of a corresponding specific physical process and chemical reaction*

Moreover, the most important point is that during such an irradiation a **concentration of “effective interaction volumes”** (e.g. **spurs** and **blobs** at water radiolysis) with characteristic size of about one mean free path of active particles should be sufficiently dense to allow these micro-volumes to **overlap each other**

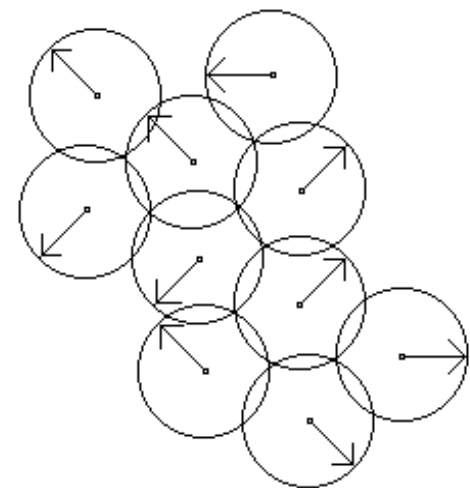
Fig. 1 a

Primary radiation



a)

Sphas of action of
secondary particles



We shall operate now with *energy* of the irradiating beam pulse and with its surface or volumetric *power flux density* at the target, which are the ‘**physical**’ characteristics of an irradiation process

Taking into consideration *mean free path* or *projective range* and *pulse duration* of the fast particles or X-ray beam photons within a target material, we shall eventually discuss the problem in terms of *concentration of fast particles within the object material during the irradiation process*, which is the ‘**chemical**’ parameter of the process

We shall show that under certain conditions the effect of short-pulsed irradiation of an object will have the essentially *non-diffusive character on initial stages*, and it may be accompanied by some synergetic and collective effects

The final result will be formed by *2 stages*, i.e. by this “instant” volumetric creation of active products of interaction (e.g. of water radiolysis) and their subsequent classical transformation and diffusion

The ***non-steady-state*** physical phenomena as well as ***non-stationary*** development of chemical processes have to be counted as an intrinsic feature of perfect flash radiation effects

New opportunities arise here thanks to recently emerged sources of pulsed radiation having high intensity

Between them one of the most perspective devices is ***Dense Plasma Focus***

Apparatus

Dense Plasma Focus (DPF) device belongs to a class of gas-discharge devices of the **Z-pinch** type

It can generate **X-rays** (both soft and hard – SXR and HXR), **plasma jets**, fast **ion** and **electron** beams, and **neutrons** as well

We used SXR in microelectronics, HXR – in radiation enzymology, and fast ions with plasma jets – in radiation material sciences

To emphasize real pulsed effects and differ them from classical phenomena we have used for the **H/SXR irradiation**:

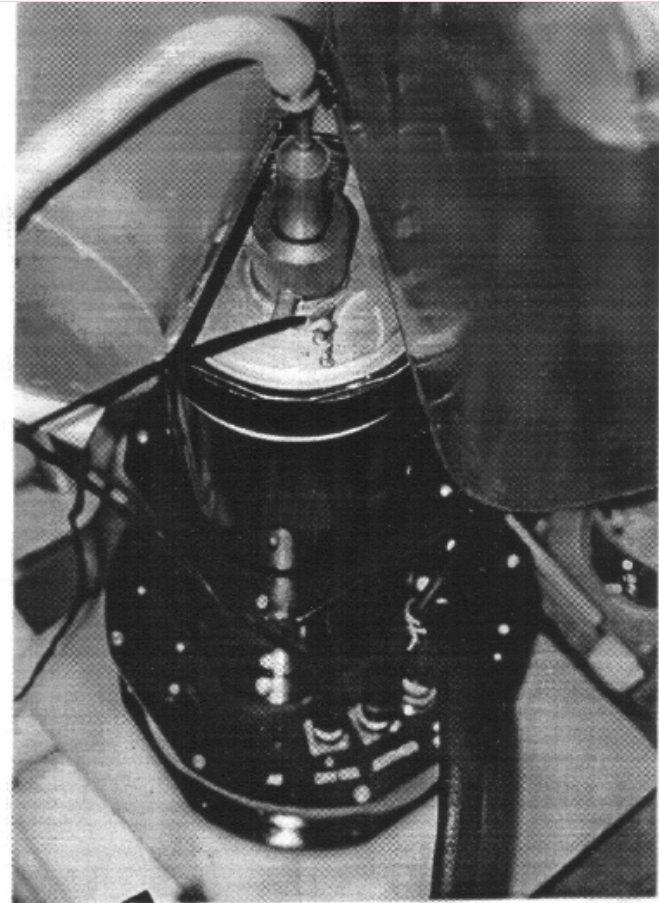
- **isotopes** - ^{137}Cs and the beta-source Sr-Y – at various time periods lasting from minutes till hours
- medical **X-ray tube** (1...100 shots, ~ 1 s) and
- several devices of Dense Plasma Focus type (1...100 shots, $\sim 1...100$ ns)

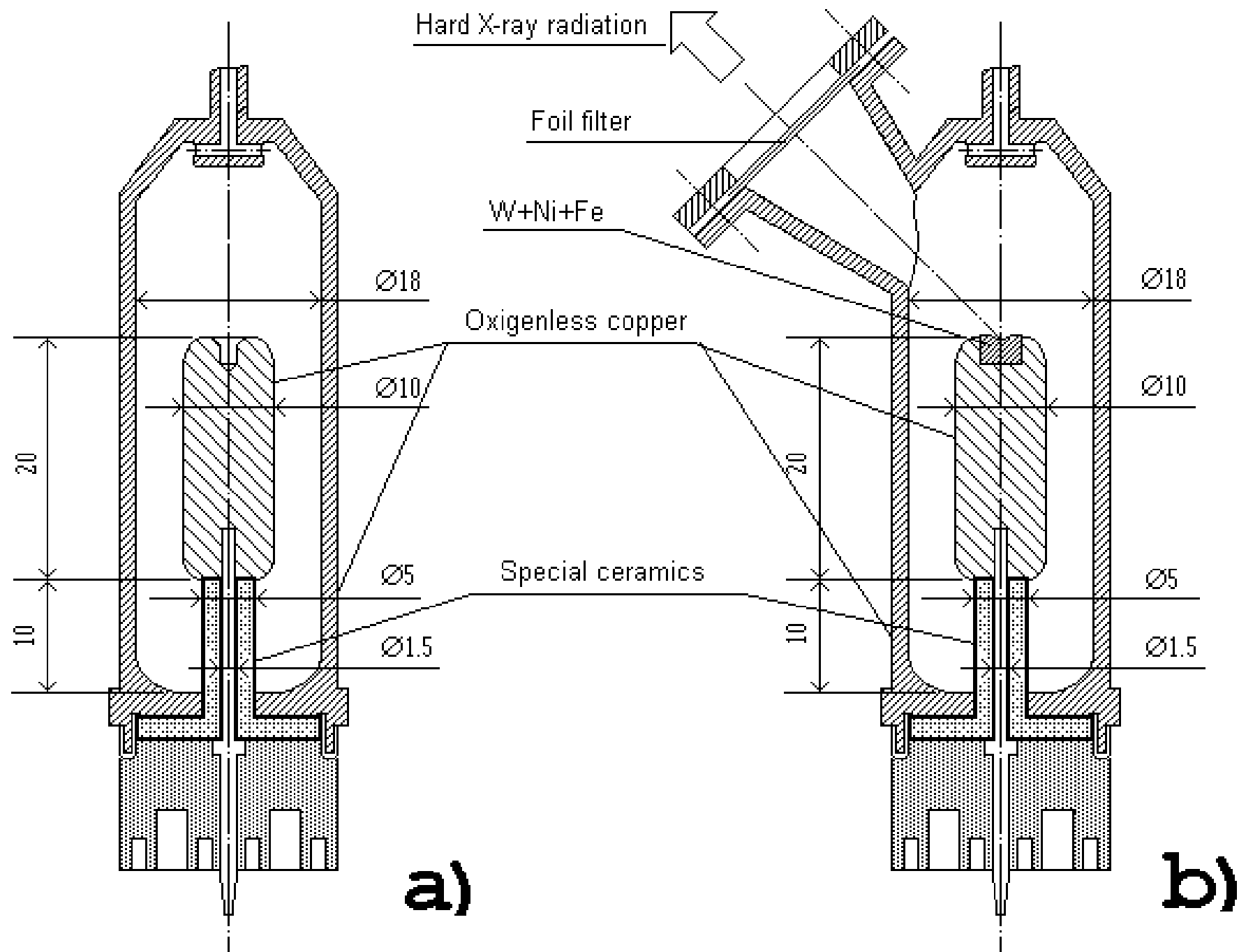
We have prepared our DPF – “PF-0.2” and “ING-103” – for applications in **biology**

These devices has been rearranged to make possible to extract from them an **X-ray** radiation having the photon energy in the range **above 7 keV**

It was made by manufacturing of a special **anode insert** as well as a **window covered by a foil**

PF-0.2





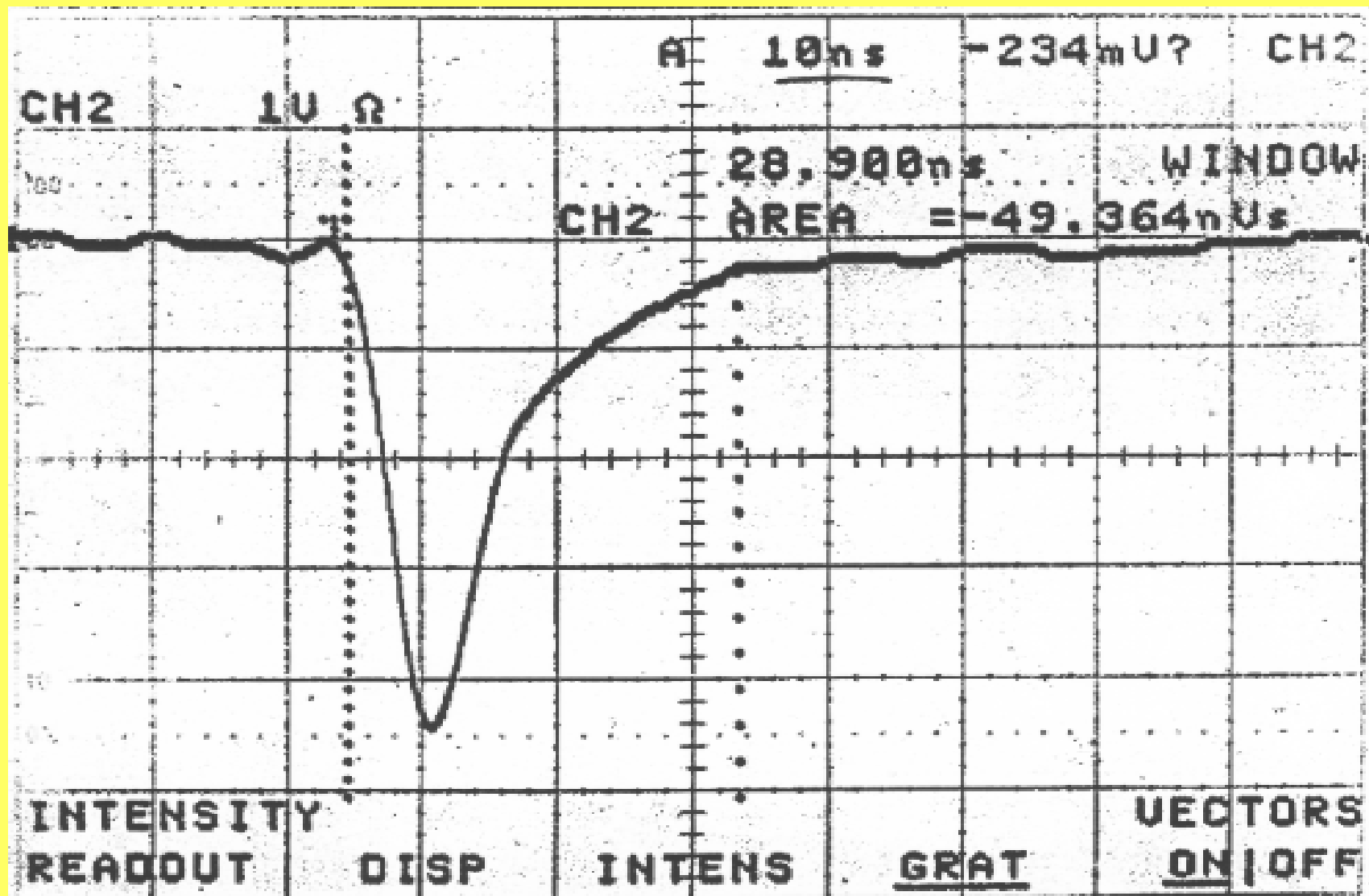
“PF-0.2” device parameters

Battery capacity	1.4 μ F
Max. discharge current	150 kA
Actuating voltage	12 – 20 kV
Energy storage (max)	0.2 kJ
Repetition rate	0.1 – 0.01 Hz
Duration of a single shot set	~1000 shots

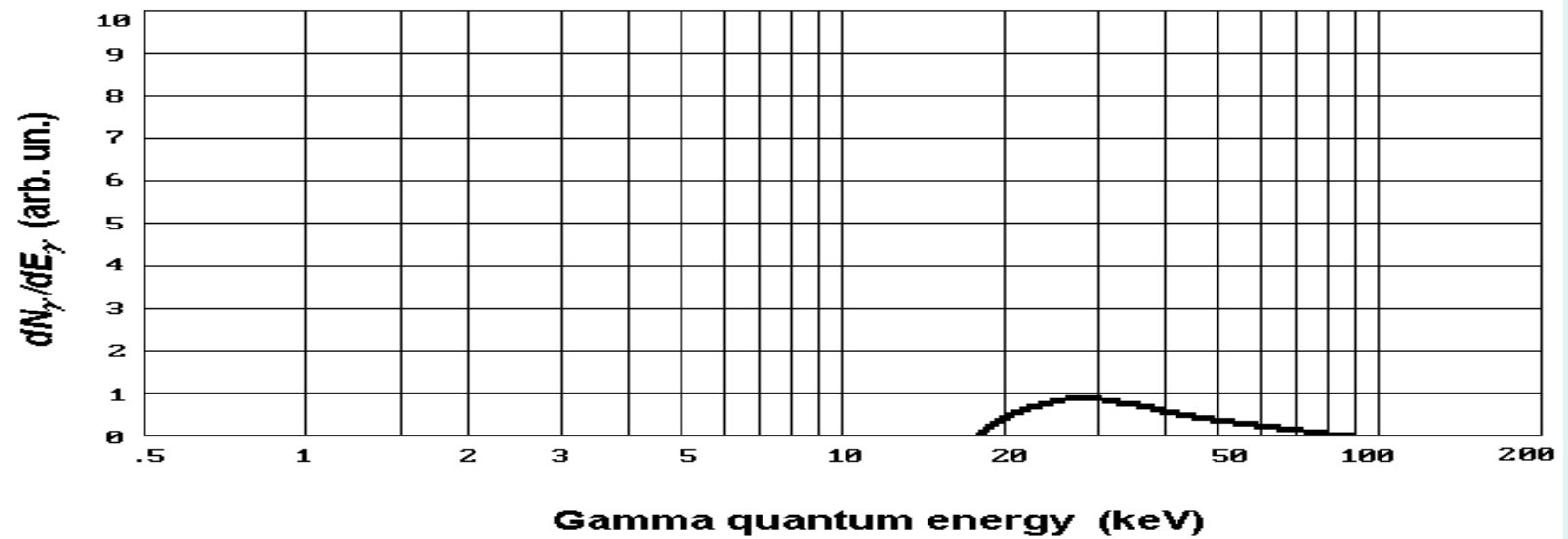
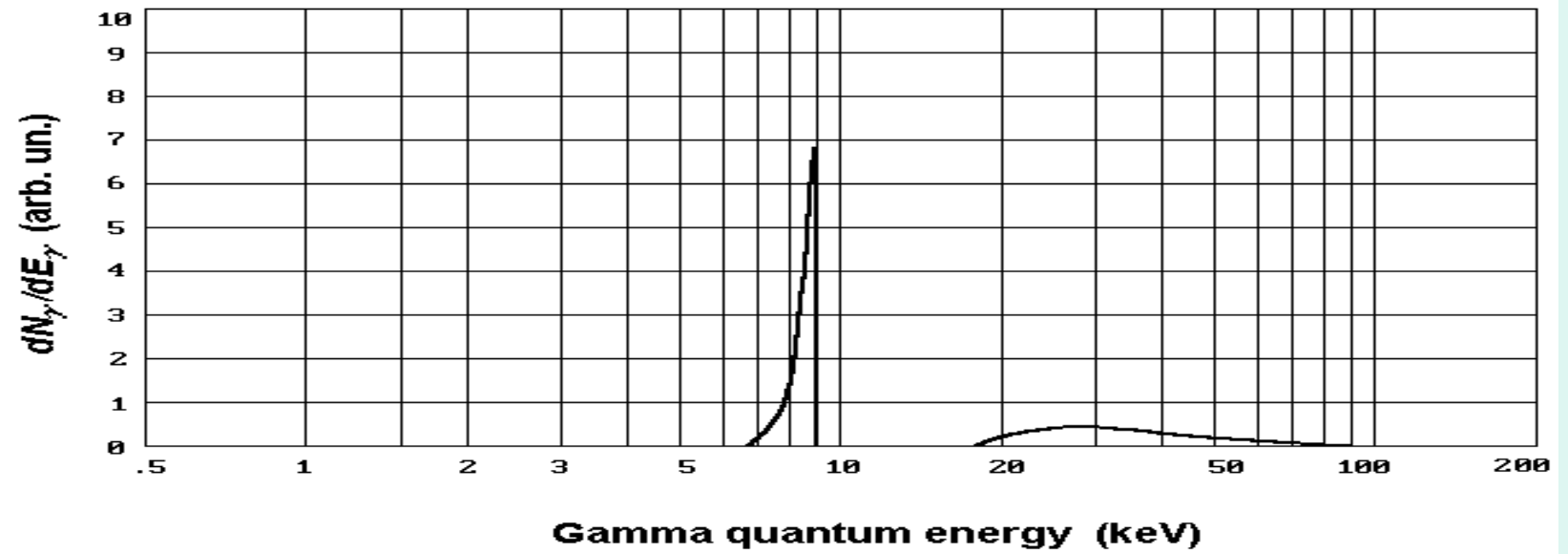
Main parameters of the X-ray radiation, which can be delivered onto a target from this our device are as follows:

- pulse duration is equal to 4 ns with the rise-time less than 1 ns
- total X-ray yield in the range of the photon energy higher than 7 keV is circa 0.1 J in the full solid angle

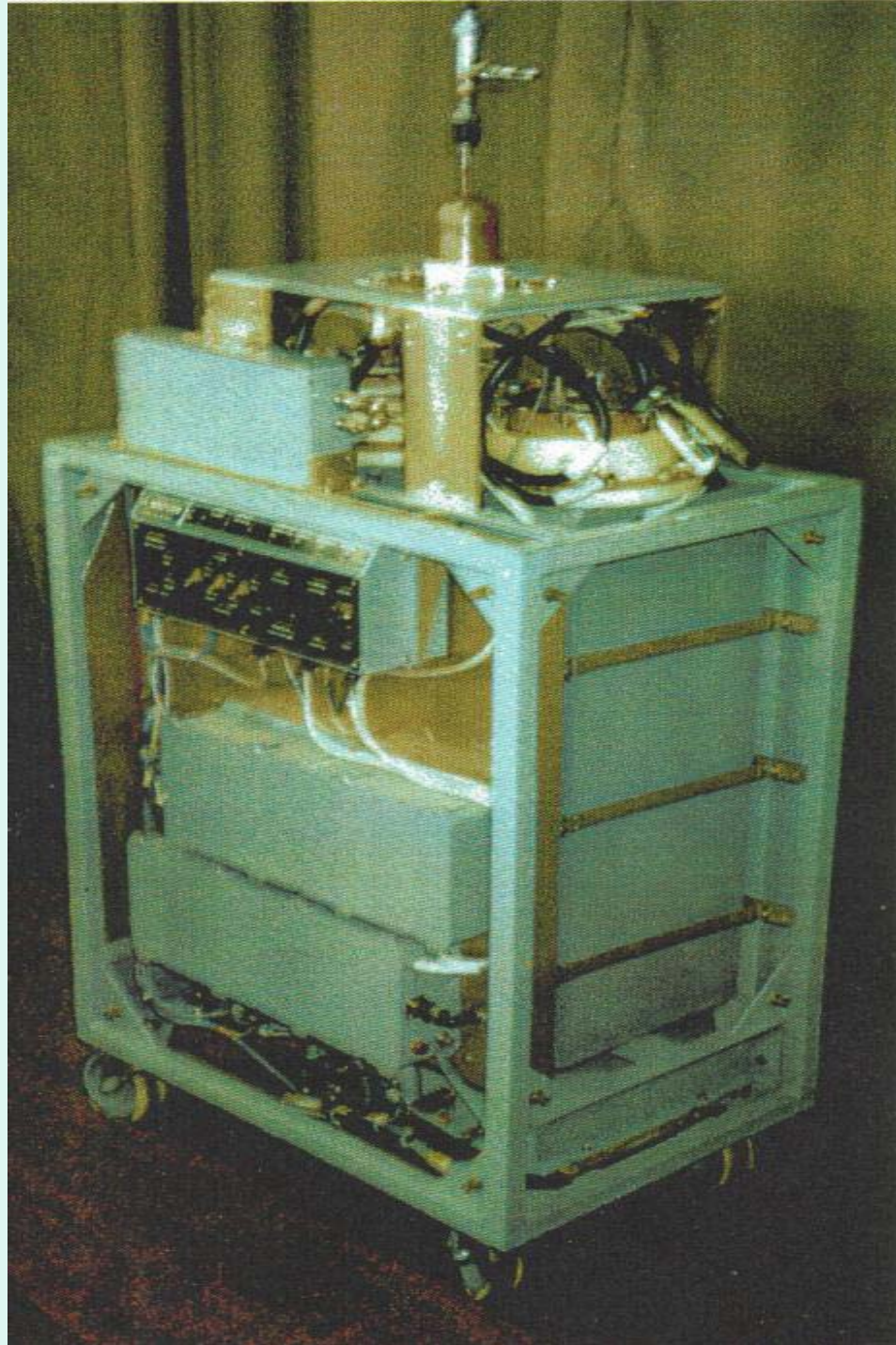
Hard X-ray and neutron pulses of PF-0.2



- **maximum** of the X-ray radiation energy is directed at the angle of ~ 50 **degrees** to Z-axis of the DPF chamber
- **spectra** of X-ray radiation extracted from the source depend on the material of foils used to cover the window of the DPF chamber, in the cases of a copper foil and with a foil made by aluminum look as follows:



ING-103



“ING-103” device parameters

Battery capacity	16 μ F
Max. discharge current	350 kA
Actuating voltage	12 – 23 kV
Energy storage (max)	5.0 kJ
Repetition rate	0.1 – 0.01 Hz
Duration of a single shot set	~1000 shots

Main parameters of the X-ray radiation, delivered onto a target from this device, are about the same as for the PF-0.2 except the following:

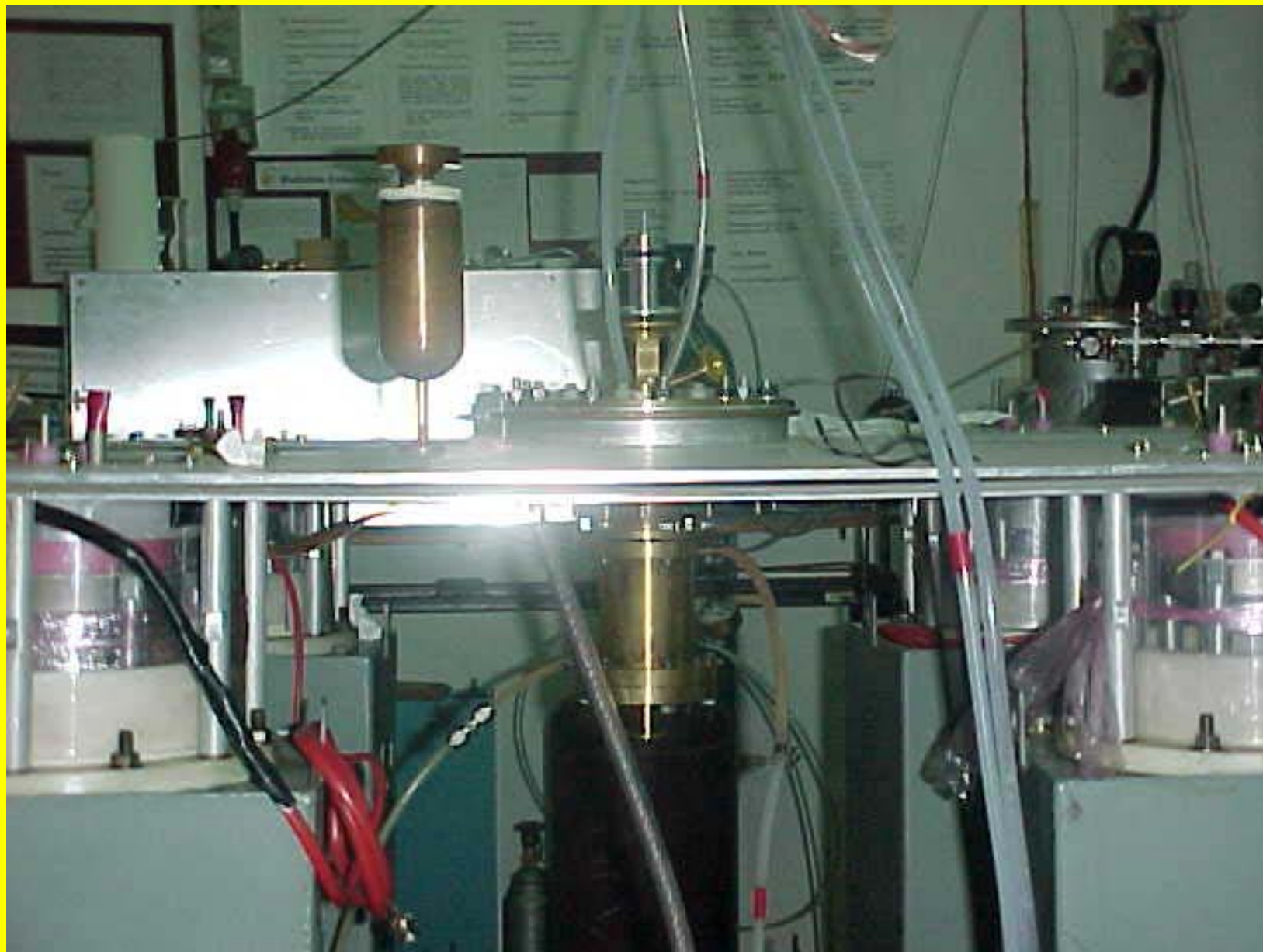
- pulse duration is equal to 10 ns with the rise-time less than 1 ns
- total X-ray yield in the range of the photon energy higher than 7 keV is circa several J in the full solid angle

For SXR irradiations used in microelectronics we operate with NX1 facility

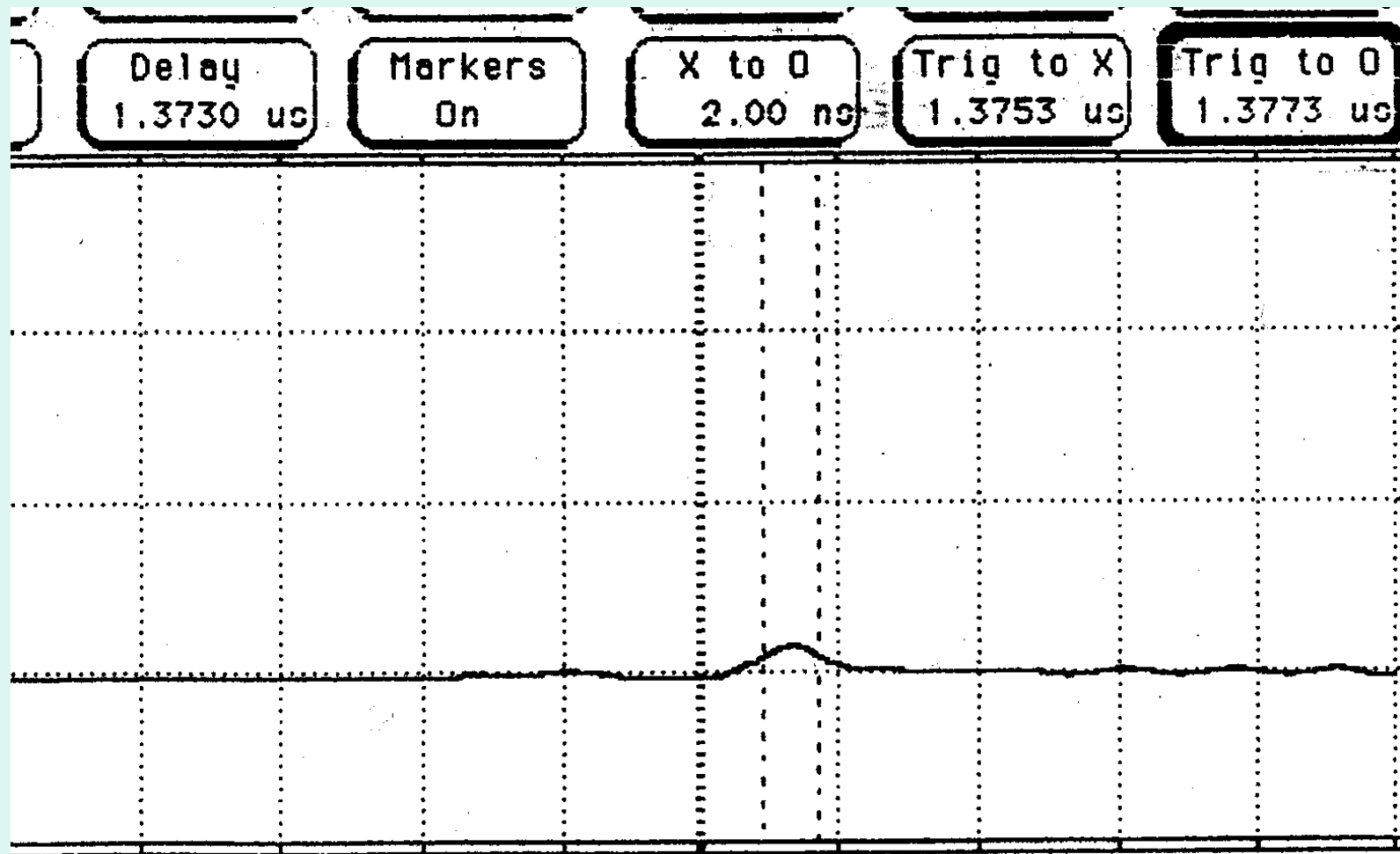
Main parameters of the SXR radiation, delivered onto a target from this device, are:

- pulse duration is equal to 2 ns
- total X-ray yield in the range of the photon energy ~ 1 keV is circa 100 J in the full solid angle

NX1 device



Hard and soft X-ray pulses of NX1

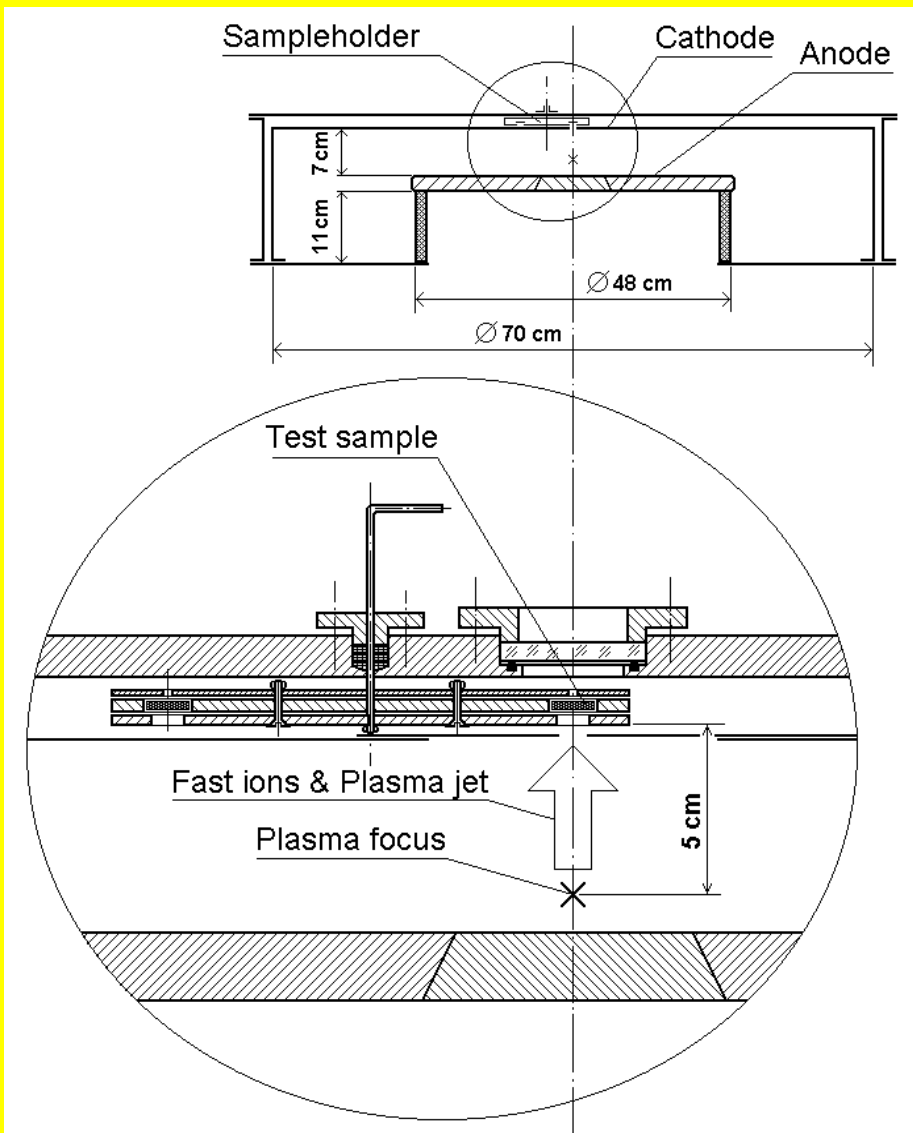


For plasma and ion beam irradiations used in material sciences we operate with PF-60 and PF-1000 facilities

Main parameters of the above types of radiation, delivered onto a target from this device, are:

- pulse durations are equal to 10...100 ns
- power flux density of plasma jet ($v > 10^7$ cm/s) and ion beam ($E \sim 100$ keV) on a target surface vary within the range $10^5 \dots 10^{10}$ W/cm²

PF-60 (FLORA facility, $E = 60$ kJ)





To clarify the impact of short pulses of ionizing radiation on physical processes and chemical reactions at the kinetic level we have to compare *parameters of the above sources* with *typical kinetic scales of interaction process* (collision rates, mean free paths, LET, diffusion length, etc.)

Characteristic scales

After physical and physics-chemical stages in radiation chemistry some chemical reactions occur in **one stage**, just at a molecule encounter, whereas another ones take place ***via a transition state***, in which reactants come together as an activated complex in a particular orientation

Reactions of the first type proceed faster in comparison with the second one, where processes of bond breaking and making are produced usually much slower

Our ultimate goal is to find situations where duration of the *radiation pulse will be of the same order as the time of a reciprocal process*

And moreover - when the number of photons or created by them secondary electrons (or ions) will be of the same order of magnitude as the number of the reaction molecules *during the above period of time*

The shortest lengths are just reactant's *molecule size* and *intermolecular distance*

Another typical kinetic length refers to a *distance traveled by a particle between collisions in gas or to diffusion path* in liquid and solid states

But at the action of ionizing radiation onto matter the important spatial scale will be a *mean free path of secondary electrons and ions* created by this radiation

One more essential parameter of interaction is **linear energy transfer** (LET), which strongly depends on a sort and energy of an ionizing particle as well as on the type of a substance under irradiation

Subsequently the **length of diffusion path** of these particles becomes important – the distance, on which they transfer to the medium by collisions say about 95% of their initial energy

And again here the distances traveled depend on the nature of particle and its molecular weight as well as on the particular substance of the medium

At the examination of the interaction process we have to take into account also a mean free path of X-ray photon inside the substance and a ***space occupied by our pulse at its interaction*** (absorption) with a substance

If mean free path for a photon is small enough then our pulse will shrink during absorption, and photon concentration will be increased in comparison with the pulse in a free space

If just contrary to this the path will be large enough then to calculate the concentration of photons we have to take into account both mean free path and the volume occupied by reagents

As for *time scale* of relevant processes taking place at the interaction of radiation with matter and for *its repetition rate* it can be presented as follows

Time scale, seconds	$10^{-17} \dots$ 10^{-13}	$10^{-13} \dots$ 10^{-12}	$10^{-12} \dots$ 10^{-9}	10^{-6}
Processes	Photoelectric absorption of X-rays, atomic and ion transitions, Auger processes, Compton effect, pairs and free radicals production, ionization, dissociation, simple ion-molecule reactions	Frequency of collisions of free electrons, its thermalization and hydration; relaxation of rotational and vibrational energy of molecules; chemical reactions of hydrated electrons	Brownian movements, diffusion of particles on traveling diffusion distances ~ 0.2 nm for particles having diameter of about 10 nm in liquids; chemical reactions	Mean distances of diffusion 6 nm for particles having diameter of about 10 nm; rate of new living cells appearance in animals; chemical reactions

Some reactions may last very long period of time: e.g. radical reactions may proceed during time intervals up to 10 s; so do for a number of physical processes, in particular connecting with a mass transfer, such as diffusion, ablation, etc.

Thus, as it may be seen, all processes connected with reagent particles themselves occur during atto-femto-picosecond intervals, whereas element and mass distribution is changed during periods of 10^{-11} s through tens of seconds. So duration of irradiating X-ray pulses have to be in the interval 10^{-13} s through 10^{-8} s, what can be reached with DPF

Chemical reactions at short-pulse radiation - factors that influence their kinetics

It is a well-known fact that there are only a few methods of increasing chemical reactivity – to increase respectively *temperature T* , *concentration C* , *external pressure p* (in all three cases to increase collision rate), and *to use catalyst* (to provide an alternative, lower energy, pathway) and *ultrasound*

But using short powerful pulses of different types of hard radiation – separately or in combination – we may increase reactivity to a greater extent

From ultrasound activation this type of reaction stimulation differs by its **'instant' volumetric** action. Indeed, for a sound and even for shock, burning or detonation waves there is a need in time *to penetrate the volume* occupied by the reactants.

Because velocity of wave of these types connects with a mass transfer they are usually of 'hydrodynamics' scale, i.e. relatively slow.

The wave traveling time usually is longer (or in the case of a detonation wave just equal) than the rate of reaction; thus the stimulation occurs **sequentially, step by step** through the system.

Just opposite to this we may **illuminate the volume practically *instantly* in all its parts** because many reactions have a relatively long period of their development in comparison with the time of light penetration and existence inside the volume

And we may use X-ray radiation for any above-mentioned method of the reaction rate increase:

- to increase ***temperature*** in many local points uniformly throughout a volume by direct absorption of radiation by reagents themselves or by some absorber centers specially introduced inside the volume,

- to raise instantly **concentration** by evaporating tiny inserts or ionizing a substance (thus producing many electrons or, e.g., radicals)
- to increase **pressure $p \sim nkT$** either because of the temperature T increase or increasing density n by production of electrons (or free radicals) due to 'instant' ionization of substance
- to release, to activate, to produce or just locally heat some **catalysts** previously encapsulated *within the volume of reagents*

And what's new in these types of 'flash influence' on the reaction rate by ionizing radiation is its switching on by non-classical - *instant and volumetric* - method

It might give various new opportunities

Let's list a few of them

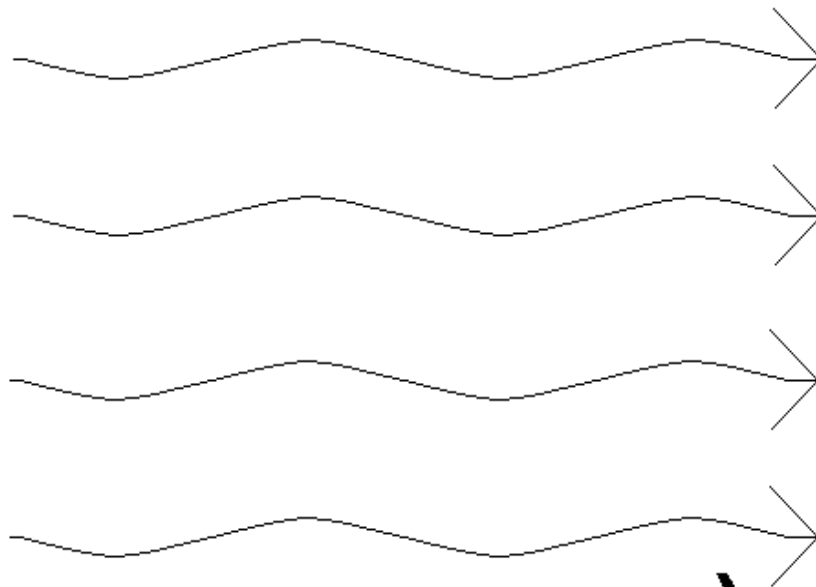
First, let's create absorption of hard radiation in many points throughout the whole volume in an explosive gas mixture in one moment (e.g. by special inserts introduced homogeneously in material)

In this case ***multiple shock waves*** (SW) can be produced also ***within the volume in one time***

Their ***interference*** (slant collisions and bouncing) will produce many local ***cumulative streams*** inside the material

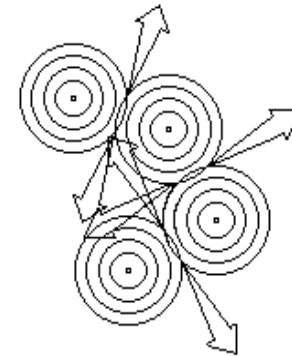
Fig. 1 c

Primary radiation



c)

Microexplosions (shock waves
with cumulative streams)



These streams will have velocities 3 to 4 times higher than their predecessors (SWs) had

This physical factor may influence *macroscopic chemistry kinetics* (mixing, reagents supply, etc.) of the explosion

Another opportunity is opened when two X-ray photons are absorbed *in one moment and in a close vicinity of each other*. They produce fast electrons or ions *not* just in two points surrounded by cold medium. Instead they create various *fast particles, which may interact with each other* directly without thermalization and diffusion

Some effects may be connected with a non-stationary chemistry phenomena already used for years in plasma chemistry

Indeed, usually reaction rate depends on concentrations of reagents, so it became slower and slower with a time

Because of this fact many processes explore multistep paths with use of various and sometimes ecologically unacceptable substances

Good relevant example is a recuperation of Uranium after its enrichment from UF-6

In this case 6 successive reactions are used

But instant ionization of the substance throughout the whole volume with help of a short X-ray flash seems make it possible to be executed in a single act

One more effect is connected with chemical processes, in which **only electrons** are needed

For a pulse of **soft X-rays** the main absorption mechanism will be the photoelectron effect (Compton and pair production effects are excluded)

Thus the energy of X-ray flash will be used directly, e.g. for dissociation (not for heating of ions)

Thus we may save energy

Very important effect may take place at the production of **free radicals** (FR)

These short-lived but highly reactive species initiate decomposition of many organic compounds, e.g. enzymes

If enzyme molecules are immersed in water medium, its irradiation by X-rays from an isotope source will produce FR chaotically **in different points of a volume and at various moments of time** separated one from another by intervals longer than their lifetime and by distances larger than their diffusion length. A vast amount of them will disappear without any reactions produced

That is because the reaction rate depends on concentrations

In a case of a continuous radiation source due to low power of the source and because of a short life of FR their mean concentration will be very low at each moment

Just opposite to it, if we shall use the same dose but *compressed within a short period of time and within a small volume*, the FR concentration *during the period of their existence* will be very high

So might be for the reaction rate

Experiments

We have tried to prove these general statements providing experiments with several types of chemical processes

First one was done on *microlithography*, where we used resists with chemical amplification (CAR)

The chemistry of the whole process (exposure, baking, development) is complex in details and encompasses a multistep, catalyzed chemical reactions in a solid film

General principle is as follows. During exposure of the resist the radiation sensitive CAR component is decomposed to acid. This acid works subsequently as a catalyst when resist is heated to 100-140°C for several minutes during a so-called Post Exposure Baking (PEB) procedure thus producing significant chemical changes in the resist. For negative CAR this means cross-linking of polymer fragments in the resist polymer structure. And for positive CAR - the destruction of base penetration inhibitor, which makes the exposed resist's zones containing the polymer fragments (typically 10^4 monomers) subsequently soluble in a developer

With the device NX1 we used photon energy spectrum concentrated mainly near 1 keV (H- and He-like resonance lines of Ne), which is optimal for the proximity X-ray lithography

Such a pulse at its interaction with the resist penetrates a depth only 1 μm ; so in this case it compresses inside the resist by many times

The emission of Auger electrons having energies ~ 280 eV is the dominant mechanism of de-exciting the carbon atom (the predominant species in a resist) once a K-shell hole is created

These electrons dissipate about a half of their energy within a sphere with a 5-nm radius around the point of X-ray absorption

Sensitivity of the resist is about 0.01 J/cm^2 . It means that circa 10^{14} photons of 1-keV energy have to be absorbed inside the volume of the resist having a thickness of about $1 \text{ }\mu\text{m}$. Total volume occupied by the irradiating X-ray photons under the area of 1 cm^2 is 10^{-4} cm^3 . Time of flying of X-rays through this $1 \text{ }\mu\text{m}$ layer is negligible – $3 \cdot 10^{-15}$ seconds. So in this volume 10^{14} X-ray photons altogether appear and exist during a time interval of about 1 ns

And they will produce not less than the same number of the above photoelectron penetration spheres of 5-nm radius, which will fill the volume totally (see Fig. 1a):

$$10^{-4} \text{ cm}^3 : V(5 \text{ nm sph}) = 10^{14}$$

From the other side the overall number of polymer fragments within this volume to be cross-linked subsequently at the PEB process is exactly the same:

$$10^{22} \text{ molecules} \cdot 10^{-4} \text{ cm}^3 / 10^4 \text{ molecules} = 10^{14} \text{ fragments}$$

I.e. the same number of functional groups (catalyst) will be activated

Production time of electrons is about 10^{-13} s

But the time of diffusion of electrons within a resist is about $10^{-12} \dots 10^{-11}$ s, which is comparable with a fine structure of our X-ray pulses. As for the diffusion time of the resist polymer fragments (having about 5 nm size and traveling for the same distances) induced by the action of X-ray radiation – it will be much longer than the duration of the whole X-ray pulse, namely about 1 microsecond

Thus using our X-ray pulse we may initiate all the primary reactions faster than its complete duration – to be said 'instantly'

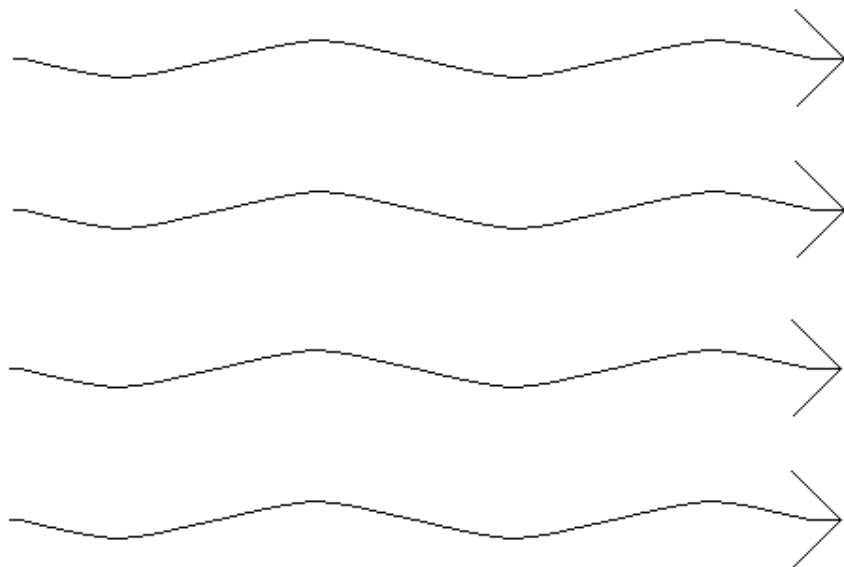
It strongly differs from the situation when we use for the same purpose just a conventional X-ray vacuum tube when we need an exposure time of continuous X-ray emission of about 15 min

In this last case *each individual X-ray photon* arrives to a certain point of a 1-cm² area of resist every 10⁻¹¹ second whereas with DPF we deposit during this interval on the same area a remarkable part of the overall energy of the pulse - *~10¹² photons*

In this way we might produce inside the whole volume of resist the partial *overlapping* electron diffusion spheres

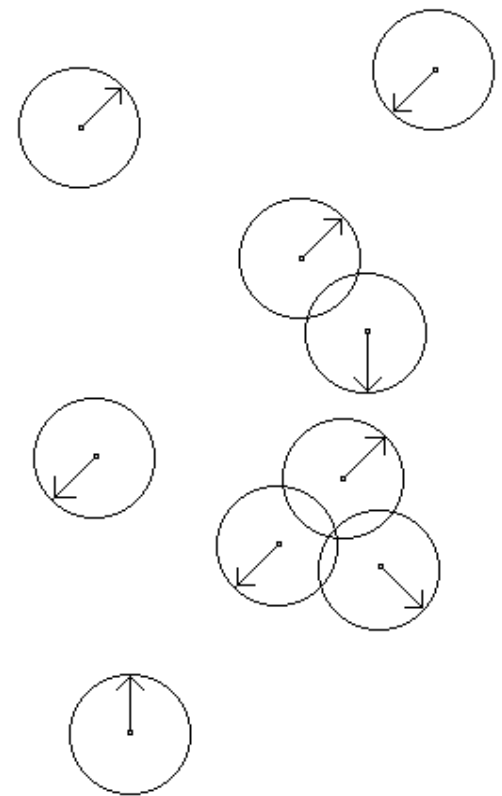
Fig. 1 b

Primary radiation



b)

Spheras of action of
secondary particles



It would result in appearance **uniformly throughout the volume** *molecules of catalyst* (acid) during a period of 1 ns

This time interval is 1000 times *shorter* than the diffusion time of the polymer fragments (diffusion is necessary for them to be cross-linked subsequently during the PEB process)

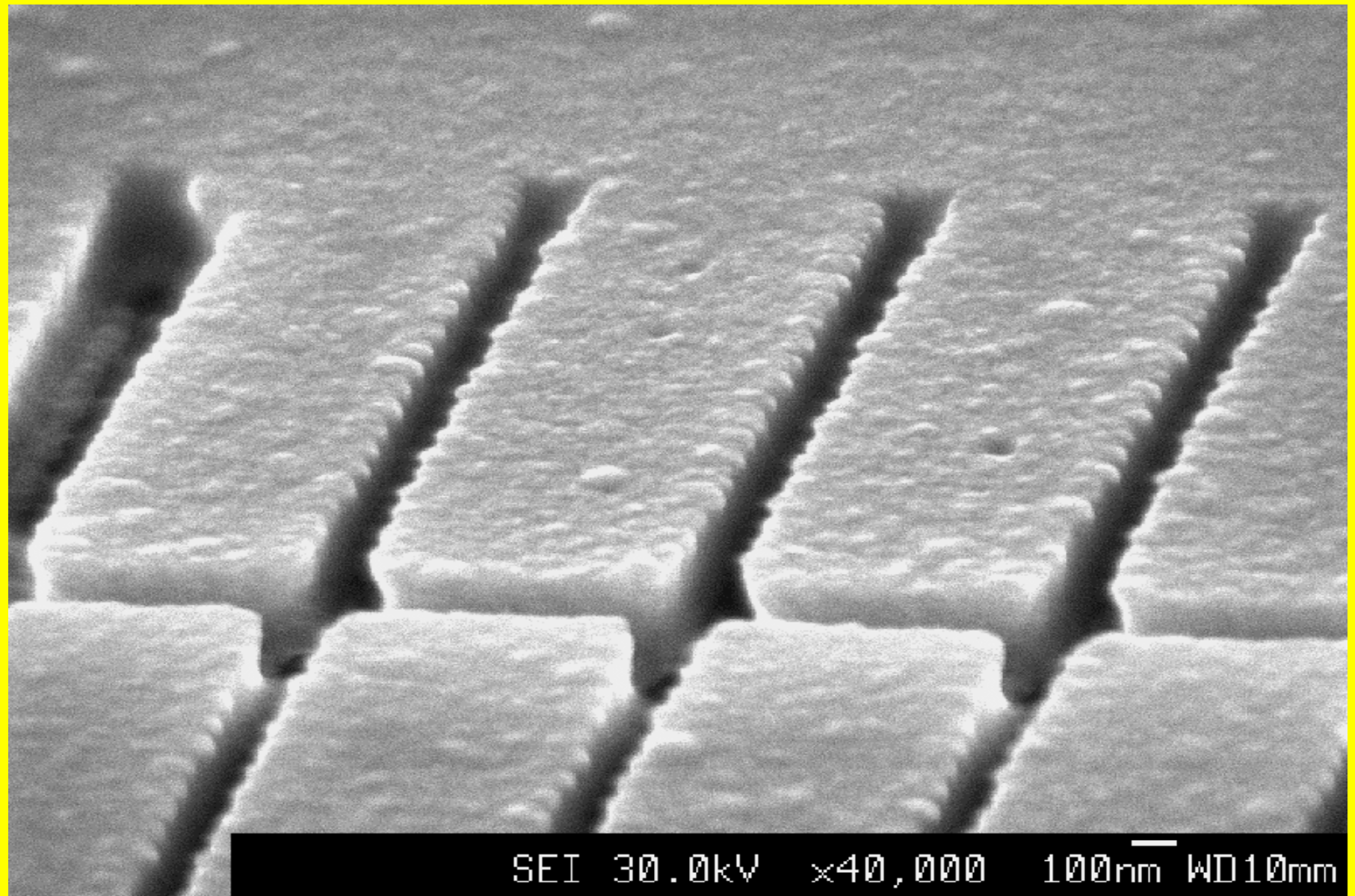
What would be the consequence of this strong distinction and what our experiments have shown?

We calculated that to collect the proper dose we would need to produce several thousands DPF shots for the resist to be exposed. It was proved beforehand in parallel by irradiation made with the conventional X-ray tube

Yet we have found in this experiment that the dose sufficient for our sample appeared to be several times less (~500 shots)

One possible explanation of this effect is that the process of decomposition of the CAR component to acid becomes more effective when *produced throughout the whole volume 'instantly'* with electrons working "side-by-side".

Fig. 2



Another example of such a process is our pulsed photography of dynamic object

In these experiments we have met at first time these phenomena. At our first attempts to take a single-shot picture of a fast rotating tyre for the goals of non-destructive quality control we have found surprisingly that all our films were overexposed. And it is in spite of the fact that we chose a dose of about the same value as it was needed for this film type under its irradiation from an industrial X-ray tube. And again eventually we have found that we need dose *several times less than it was foreseen*

Third example relates to our experiments in *material science*

In this case we irradiate our specimens mainly by deuterium **plasma jets** having velocity $\sim 3-5 \cdot 10^7$ cm/s and by **fast ion beams** (also deuterons) of circa 150 keV energy. We used them separately or in combination for treatment of surface layers of various materials (chiefly low activated stainless steels)

Our main interest lies in investigation of implanted deuteron distributions by depth inside specimens as well as in a character of modification and destruction of their surface

From one side the deuterons in steel have a very **small projective range** and consequently **large LET** (higher than 200 keV/ μm)

From the other side both types of deuteron streams have **very high power flux density** attainable with our DPF of FLORA facility and PF-1000 (up to 10^{10} W/cm²)

Thus our goal – to produce radiation defects throughout the whole volume during the period shorter than the characteristic time of a physics-chemical process – can be fulfilled in this case. We have found several unexpected effects

First we have found that the concentration peak of the implanted deuterons is positioned at some distance from a surface inside a specimen

It was in contrast to a classical implantation distribution accomplished by a continuous source of ions where it decreases monotonically from a surface into a bulk of a specimen

This phenomenon can easily be explained taking into consideration that diffusion time for gas inside the heated and melted layers of steel is much longer ($> 1 \mu\text{s}$) than the pulse duration of our deuteron streams ($\sim 100 \text{ ns}$)

That is why the distribution, which has been formed initially as the classical one during a hundred ns, ***changes subsequently***

It takes place during the cooling and solidification processes *lasting a microseconds time period because of diffusion, directed inside the bulk of the material and outwards* through the sample's surface to the gas phase

Second effect was a so-called **"broken implantation"**

This part of our work deals with **testing** of radiation resistive materials intended for use in thermonuclear fusion chambers

Usually when ion/plasma streams having emergency power flux density strike a plasma-facing component of a fusion device (tokamak or walls of a chamber for an inertial confinement fusion) a so-called **"detachment"** effect takes place (protection of a surface from the streams by a cloud of cold plasma evaporated in the very beginning of the interaction)

Just contrary to it we have found that if the same dose (fluence) of deuterons would be impinged into a specimen with the short pulse ($P \sim 10^9 \dots 10^{10}$ W/cm²), the above cloud would not protect the surface

The reason is that this cloud **absorbs high amount of energy during the time interval, which is shorter than the time of heat loss**; thus its temperature rises very much

And because Coulomb cross-section decreases with temperature, this cloud becomes **transparent** for the irradiating plasma streams

Both these effects are **impossible at the same value of deuteron fluence injected under low power flux density of the streams**

The last experiment belongs to a branch of radiobiology – *radio-enzymology*

Our experiments has been devoted to irradiation of several types of enzymes *in vitro* with differing dose, dose power and spectrum of X-rays

Measurements of the enzyme's *activity* were performed with 2,2'-azino-bis(3-ethyl-benzothiazoline-6-sulfonate) (ABTS) as substrate using Shimadzu UV 120-02 *spectrophotometer* at 25°C

Our *materials* were: **ACE** (an isolated and purified electrophoretically homogeneous angio-converting enzyme, ACE - MW 180 kDa - from bovine lungs) and **Peroxidases** - native horseradish peroxidase C (HRP, MW 44 kDa) purchased from Biozyme, and recombinant wild-type HRP (MW 34 kDa) produced from *Escherichia coli* inclusion bodies by the method developed by us earlier

ACE contained circa 98% of active molecules as determined by stoichiometric titration with a specific competitive inhibitor

ACE enzymatic activity was determined with 10^{-5} M carbobenzoxy-L-phenyl-alanyl-L-histidyl-L-leucine (Cbz-Phe-His-Leu) (Serva) as a substrate in 0.05 M phosphate buffer, pH 7.5, containing 0.15 M NaCl, 25°C, using o-phthalaldehyde modification of His-Leu as a reaction product

The measurements of *peroxidase activity* was performed with 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) as substrate using Shimadzu UV 120-02 spectrophotometer (Japan) at 25°C by the following method:

0.05 mL of ABTS solution (8 mg/mL) and aliquot of the enzyme were added to 2 mL of 0.1 M Na-acetate buffer (pH 5.0); the reaction was initiated by the addition of 0.1 mL of hydrogen peroxide (100 mM); a molar absorptivity of ABTS oxidation product was taken equal to 36800 L/mol/cm at 405 nm

Irradiation

We have used several sources of X-ray radiation in the dose range 10^{-6} through 10^2 Gy within dose power limits $10^{-2} \dots 10^6$ Gy/s, determined by an exposure time (isotopes) or a pulse duration and a number of shots (DPF):

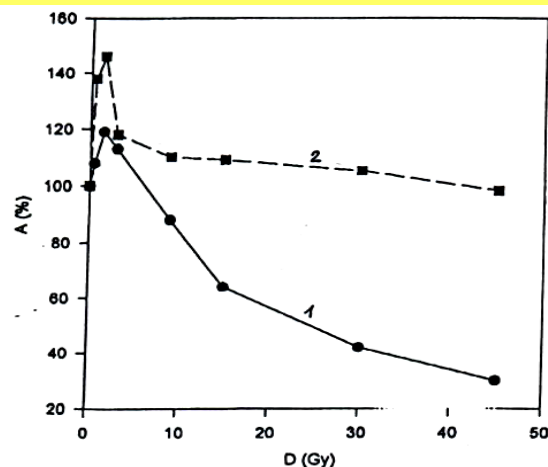
- *Standard γ -source ^{137}Cs* : $E_{h\nu, \max} = 662 \text{ keV}$, $D = 0.1 \dots 200 \text{ Gy}$, $P_D = 5 \times 10^{-2} \text{ Gy/s}$ (from seconds till hours)

- *Standard medical X-ray tube* working in 3 regimes: $U_{tube} = 50.0, 60.0$ and 90.0 keV, $E_{h\nu, max} \leq 35.0, 40.0$ and 60 keV correspondingly, pulse duration of X-rays $\sim 0.1...1.0$ s, number of pulses at a séance – $1...10$, $D = 10^{-4} - 10^{-1}$ Gy
- *Isotope calibration β -source* of DRG3-01 (Sr-Y) with the X-ray energy spectrum in the range of $8...2000$ KeV at various time periods lasting from minutes till hours; its dose power is much less than 10^{-3} Gy/s

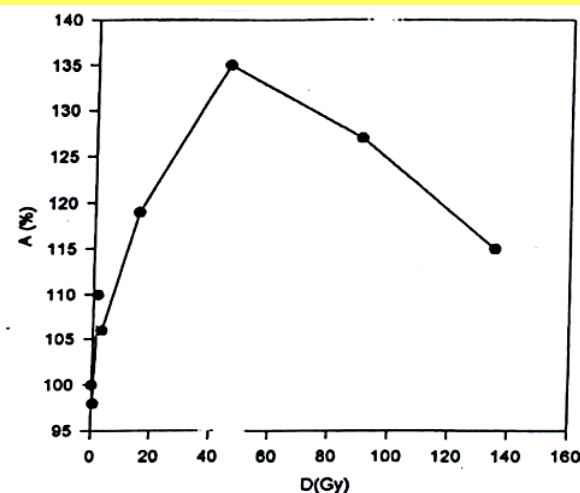
- *Miniature DPF device “PF-0.2”*: $E_{h\nu, max} \geq 7...100$ keV, X-ray pulse duration – 2 ns, X-ray yield $\sim 0.1...1.0$ J/shot, $D = 10^{-6} - 10^{-3}$ Gy/shot, neutron yield $\sim 10^6$ n/pulse ($E_n = 2.45$ MeV), $P_D \sim 10^{3-6}$ Gy/s
- *Medium-size DPF device “ING-103”*: energy storage - 2.0 kJ, $E_{h\nu, max} \geq 7...200$ keV, X-ray pulse duration ~ 10 ns, X-ray yield $\sim 1.0...10.0$ J/shot, $D = 10^{-5} - 10^{-2}$ Gy/shot, neutron yield $\sim 10^8$ n/pulse ($E_n = 2.45$ MeV), $P_D \sim 10^{3-10}$ Gy/s

Both DPF sources were used at various distances and with one to 100 times irradiation ('shots') per séance for a specimen, with two types of X-rays filters – Al and Cu foils, and with two types of n/γ filters – transparent for X-rays and opaque for neutrons or – in contrary – transparent for neutrons and opaque for X-rays

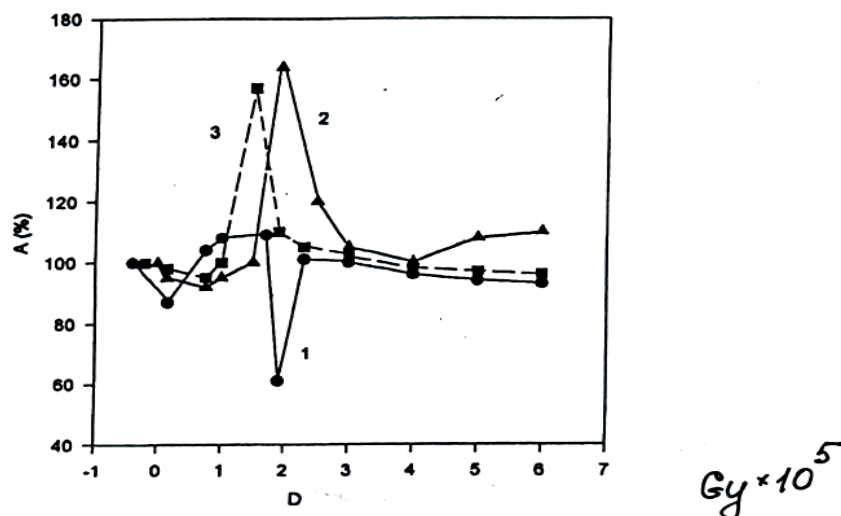
Results



γ -Irradiation induced changes in horseradish peroxidase catalytic activity. native HRP; 2, recombinant HRP pretreated with $10^{-6} M H_2O_2$. $10^{-7} M$ enzyme solution in acetate buffer, pH 6.0, substrate quaiacol.



γ -Irradiation induced changes in tobacco peroxidase activity. $10^{-7} M$ enzyme solution in acetate buffer, pH 6.0, in the presence of $5 \times 10^{-2} M CaCl_2$, substrate- quaiacol.



DPF X-irradiation induced changes in enzymatic activity (Cu-filter, single pulse): 1, native HRP, $10^{-7} M$, phosphate buffer, pH 6.0, substrate ABTS; 2, ACE, $10^{-6} M$, phosphate-borate buffer, pH 6.5, substrate Cbz-Phe-His-Leu; 3, ACE, $10^{-6} M$, phosphate-borate buffer, pH 7.5, substrate Cbz-Phe-His-Leu.

The main differences between changes in activity of the enzymes irradiated by isotope ^{137}Cs γ -sources (a&b) and the ones illuminated by PF-0.2 (c) are:

Although the amplitudes of the activity changes are about the same in all cases, the changes are measurable in the Cs-source case only at doses above 1.0 Gy. In the DPF case, however, irradiation is registered at a dose less than five or six orders of magnitude. But the dose power in this case was 4-5 orders higher

- When the dose was **decreased** below the above 2 critical levels (isotope – lower than 10^{-1} Gy, and DPF – lower than 10^{-5} Gy) no changes in enzyme activity were detected
- As expected, an **increase of dose** in the case of isotope irradiation was resulted in the complete enzyme inactivation. Contrary to that, the dose increase under the DPF irradiation during one shot – by 1...2 orders of magnitude – shows that the activity of both enzymes does not change, i.e. became the initial one

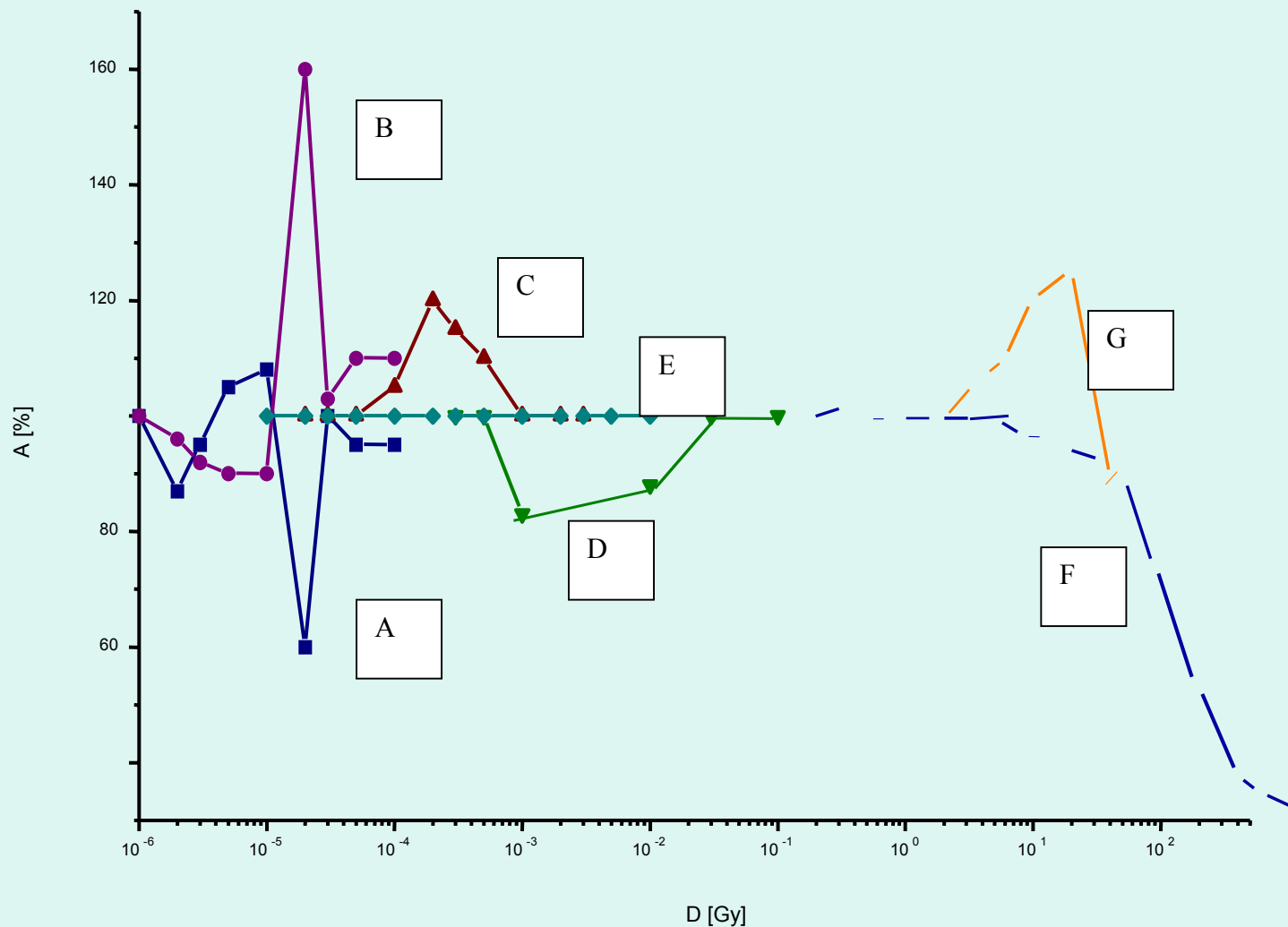
To clarify the situation, we checked *at first* the **influence of neutrons** on the results by using of special filter. This experiment did not show any appreciable effect of neutrons on the activity of enzymes in this case

Second, in case of the use of **classical X-ray tubes** for irradiation in the dose range of 10^{-5} through 10^{-1} Gy the only exception was found when we have made irradiation at the **lowest voltage** at the X-ray tube (50 kV). In this case in two experiments we have found the weak peak of the same character

Third, we changed the X-ray dose from the DPF source in ten times by increasing the distance from the source (PF-2.0 in this case) likewise for the dose power as the pulse duration was not changed. At the same time we increased a number of shots.

However, the effect appears at a dose of **100 times greater – not 10 times** as it was expected (at about 2×10^{-4} Gy) than in the case of higher dose power

Finally we have found that at changing the **Cu** filter into the **Al** one all attempts to repeat the above results have been **failed**



A, B – “PF -0.2”, Cu filter; **C** – “PF -2”, Cu filter; **D** – X-ray tube: $U = 50.0$ kV, $E_{h\nu, max} \leq 35.0$ keV; **E** – isotope β -source Sr -Y: 8 keV $> E_{h\nu} > 2000$ KeV; and “PF -0.2”, Al: 8 keV $> E_{h\nu} > 100$ keV; **F, G** – γ -source ^{137}Cs : $E_{h\nu, max} = 662$ keV

The particles of the predominant importance in the radio-enzymology reactions are *free radicals (FR)*

Their mobility is much less than this for electrons, so its *diffusion time in our water solution is comparable with the X-ray pulse*

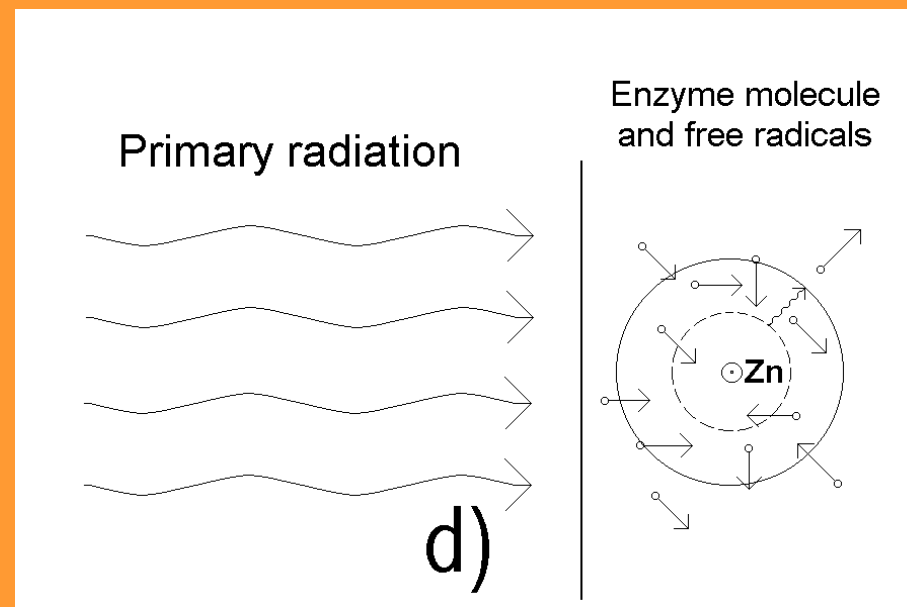
Also it is important to mention that the enzymes with the strongest activation/inactivation effects had atoms of Zn or Fe in their structure

The spectral *absorption curves of Zn and Fe atoms overlap with the Cu K-edge curve* strongly irradiated by our DPF

Therefore it is reasonable to suppose that a **presence of an atom of Zn in ACE and of Fe in HRP** might favor the above activity oscillation

Analysis has shown that our ionization zones – **blobs** – are overlapped

I.e. density of radiolysis water products is highly increased during the period of X-ray pulse:



Furthermore, this overlapping takes place during the time interval (few nanoseconds), on the order of the time intervals ($10^{-12} \dots 10^{-8}$ s) of the creation of water radiolysis products

However, it is much less than the end of reaction with radicals (10^{-6} s)

Therefore ***all the products*** instantly start to diffuse and interact with exited enzyme molecules, not with each other, as the enzyme molecule is very large
It probably explains the effect registered.

Conclusions

Pulses of ionizing radiation having duration compared or less than relevant reaction time may influence the chemical reactions on kinetic scales

Because ionizing particles or X-ray photons occupy during this period of time the whole reactor volume, the effects become of 'instant' volumetric nature

Immediate results of these two factors are an increase of reaction rate, decrease of necessary dose and possibility to fulfill some 'forbidden' reactions by means of a strong non-stationary manner of its excitation at a kinetic stage

Thank you!