

# Analiza materialelor prin difractometrie de radiatii X

## Curs 2

**Difractometrul D8 ADVANCE Bruker:  
performante si posibilitati de investigare a proprietatilor materialelor.**

- 📄 **D8 ADVANCE Bruker: prezentare generala**
- 📄 **Instrumentatie: tuburi filtre, monocromatoare, fante, detectori**
- 📄 **Metode de analiza**
- 📄 **Prepararea probelor**
- 📄 **Preluarea rezultatelor**

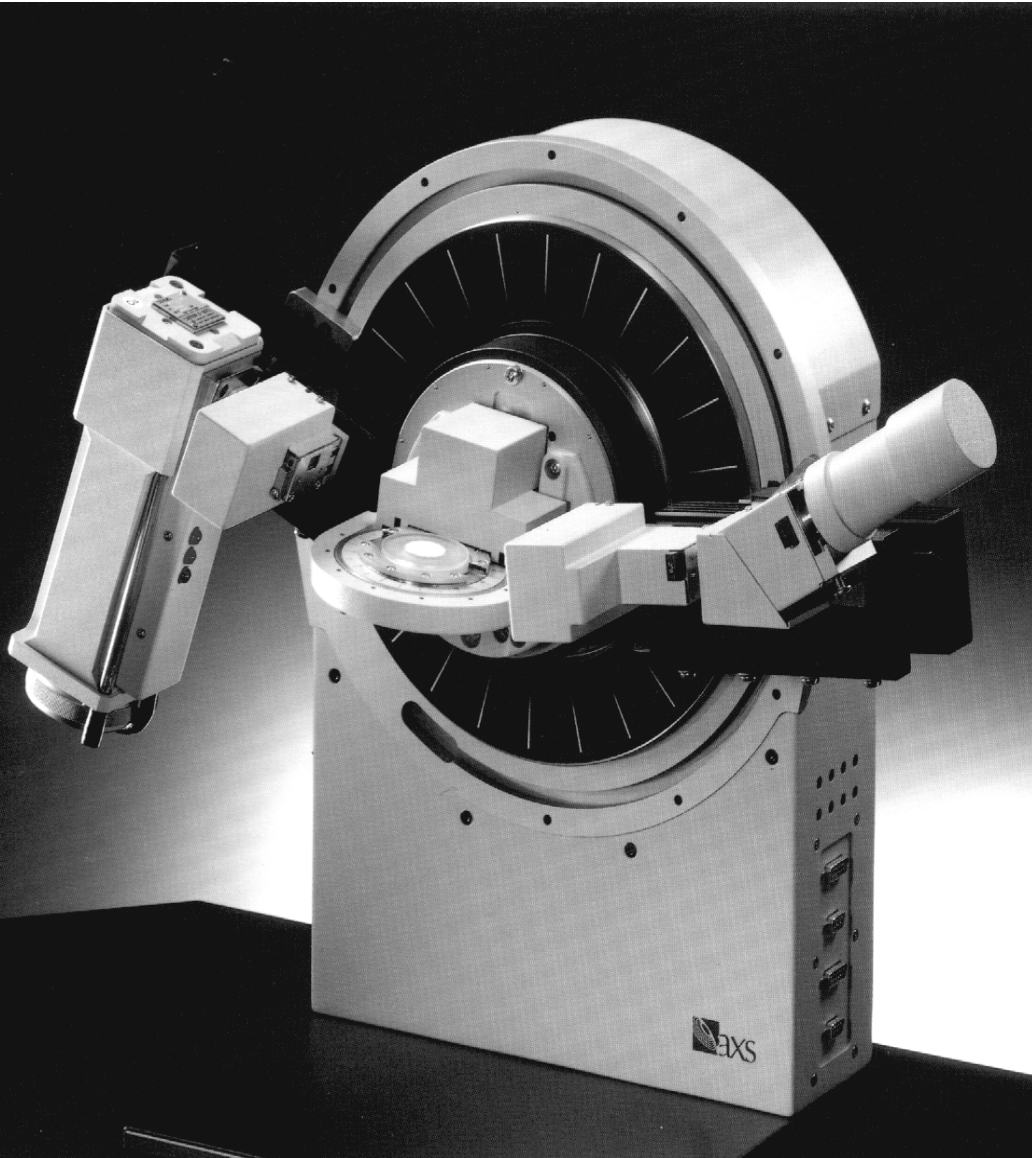
# D8 ADVANCE Bruker (1)



**D8 ADVANCE Bruker (2)**



## **D8 ADVANCE: Instrumentatie (1)**

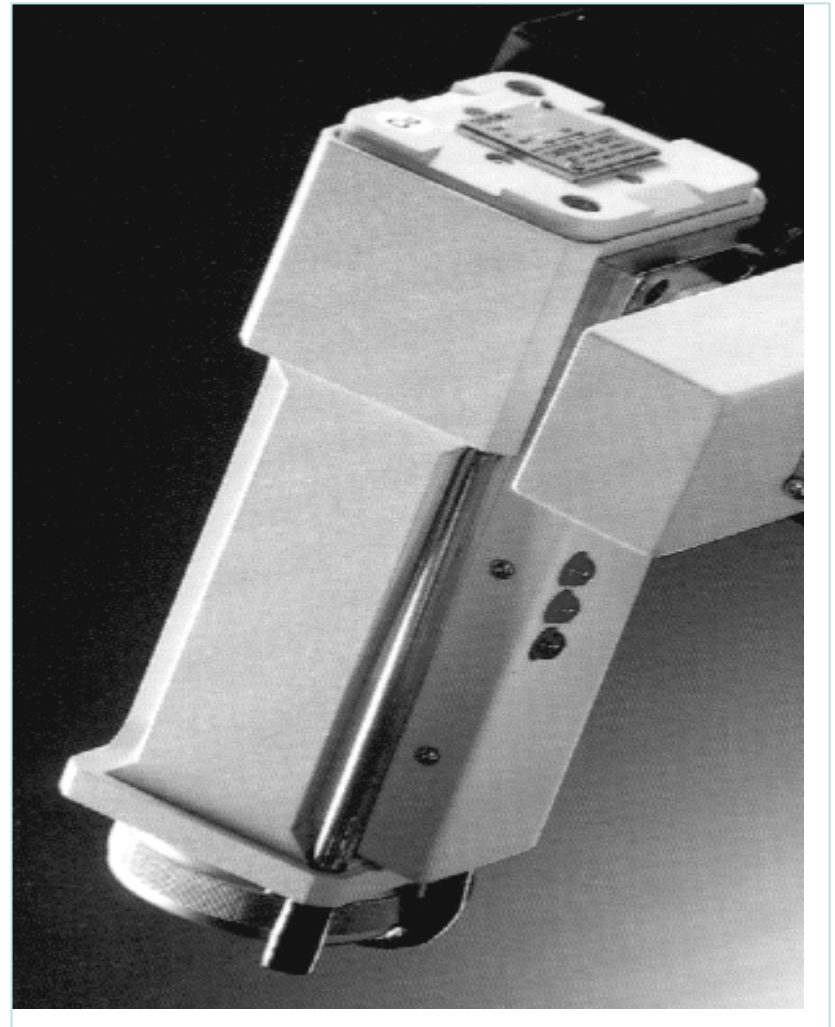


- **Radiation source**
- **Primary beam monochromator(s)**
- **Primary beam slit(s)**
- **Sample attachment**
- **Secondary beam slit(s)**
- **Secondary beam monochromator**
- **Beam tubes**
- **Detector**
- **Goniometer**
- **Electronic control unit**
- **Water supply**
- **Radiation shielding**

## D8 ADVANCE: Instrumentatie (1)

### Tubul de radiatii X:

- tip: fix, ceramic
- focalizare: long-fine
- model: Siemens KFL CU 2K
- anod: cupru
- putere 2200 W;  $U < 60$  kV;  $I < 50$  mA
- racire: apa, 5,5 l/min
- focar:  $0,4 \times 12$  mm
- fascicul:  $0,04 \times 12$  mm;  $6^\circ$
- timp de viata: 2000 ore

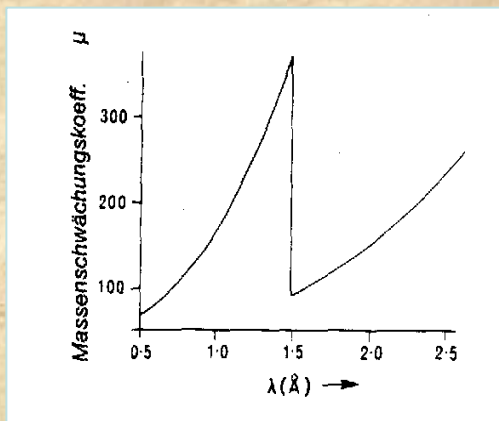
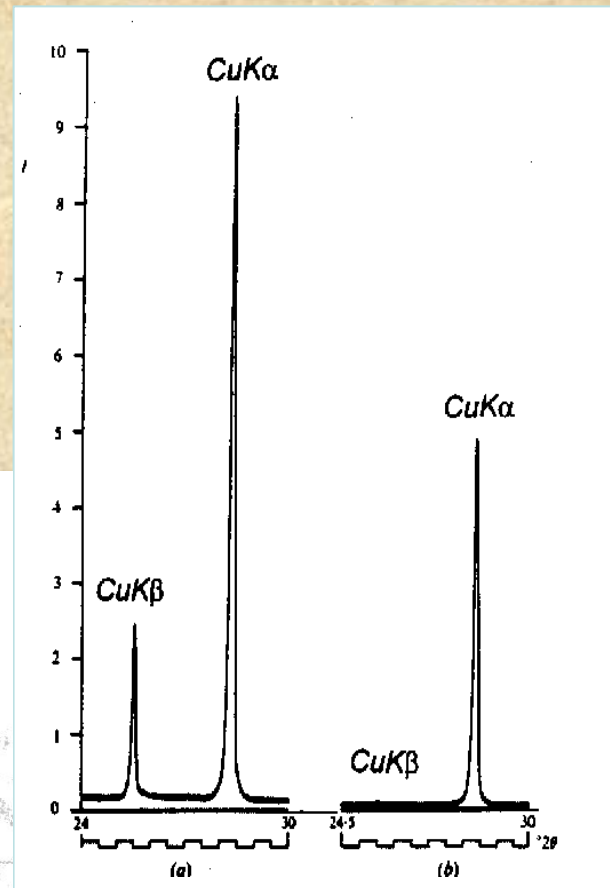
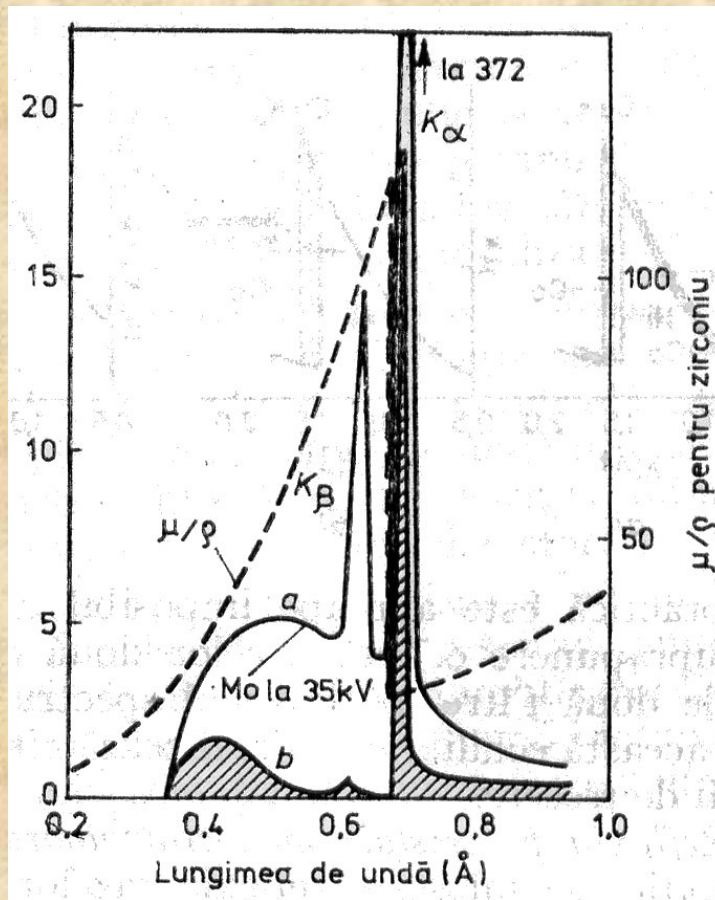
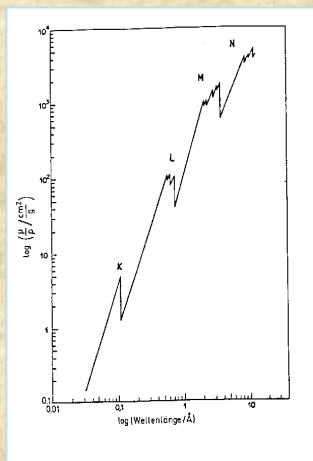


# D8 ADVANCE: Instrumentatie (2) Filtre

-radiatie Cu

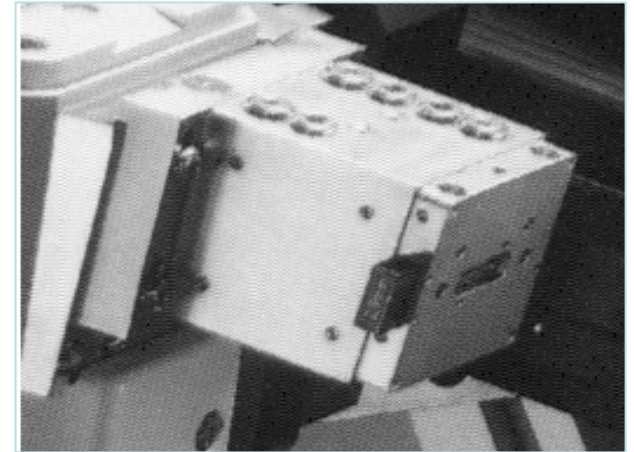
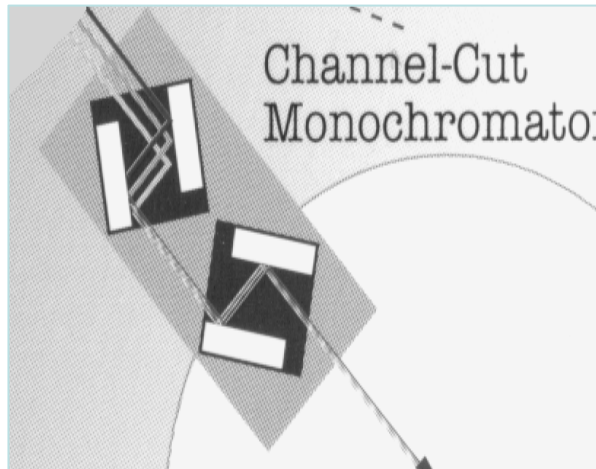
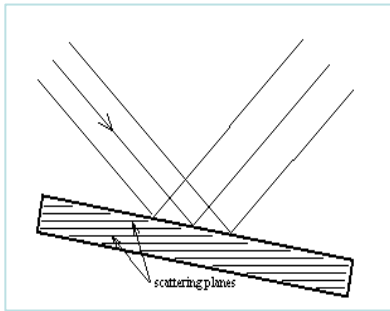
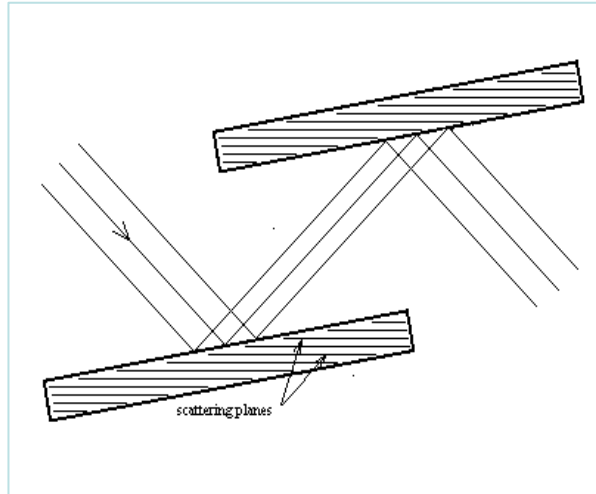
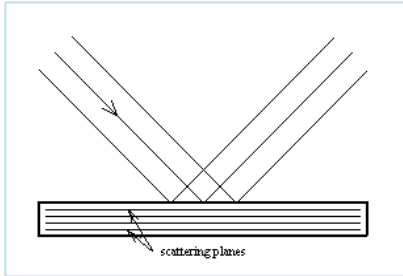
- folie 0.02 mm Ni

-  $I_{K\beta}:I_{K\alpha}$  to 0.2% (initial 16%.)

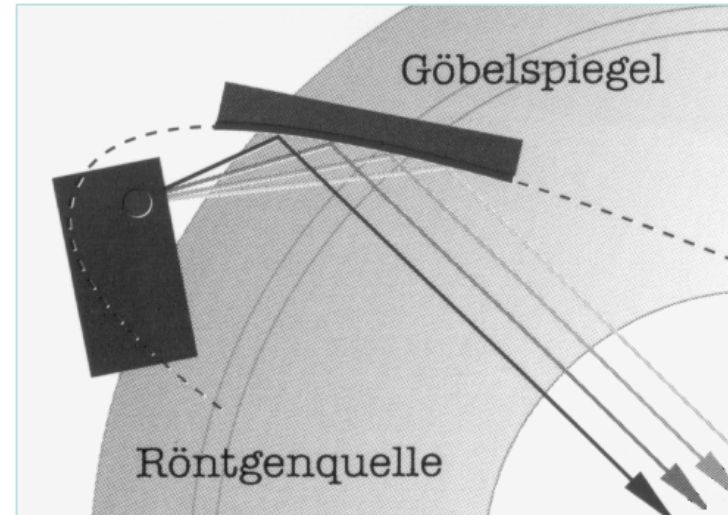
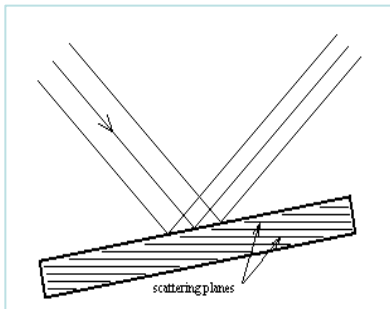


# D8 ADVANCE: Instrumentatie (4) Monocromatoare

- cresc rezolutia, scad intensitatea



**Oglinda Goebel; cristal curb  
fascicul: divergent  $\Rightarrow$  paralel**

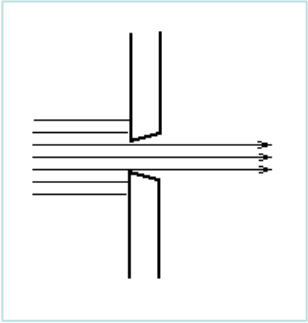


## D8 ADVANCE: Instrumentatie (5) Fante (Slits)

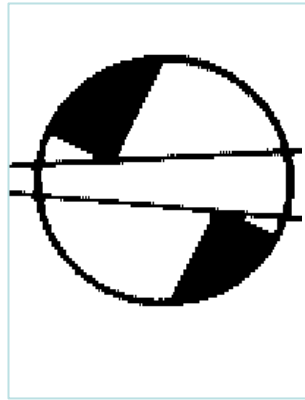
- importante in obtinerea acuratetii difractogramei in raportul rezolutie / intensitate
- soft: “vad” suprafata diferita

fixe

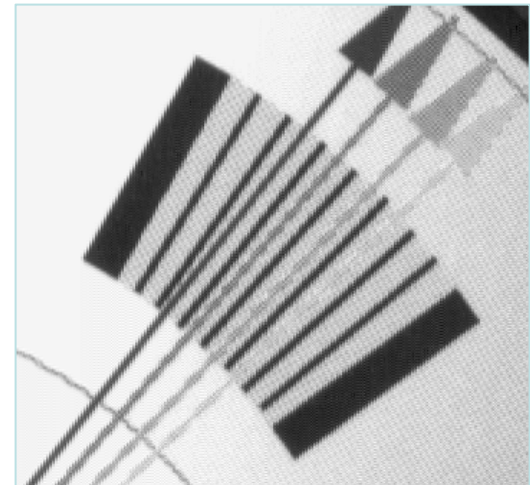
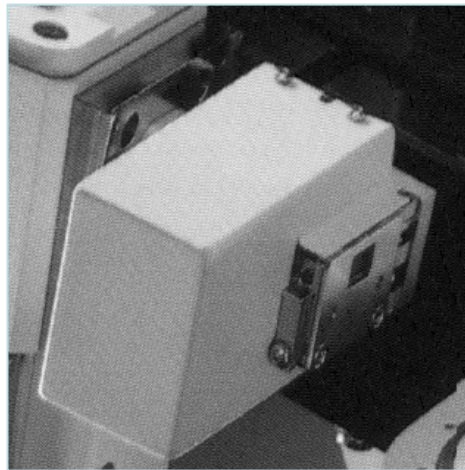
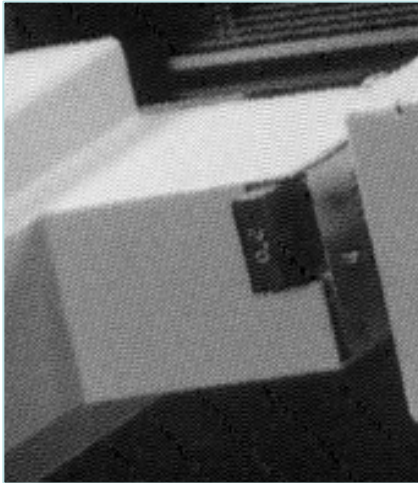
0,1; 0,2; 0,6; 1,0; 2,0; 6,0 mm



variabile



Soller



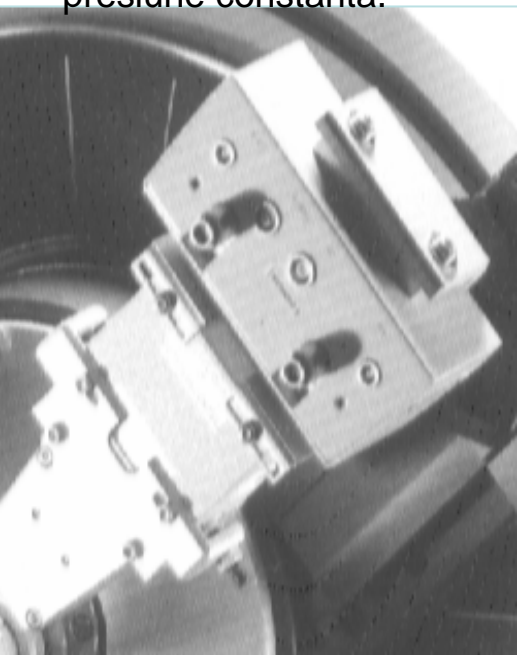


# D8 ADVANCE: Instrumentatie (6) Detectori

➤ importante in obtinerea acuratetii difractogramei in raportul rezolutie / viteza / timp mort

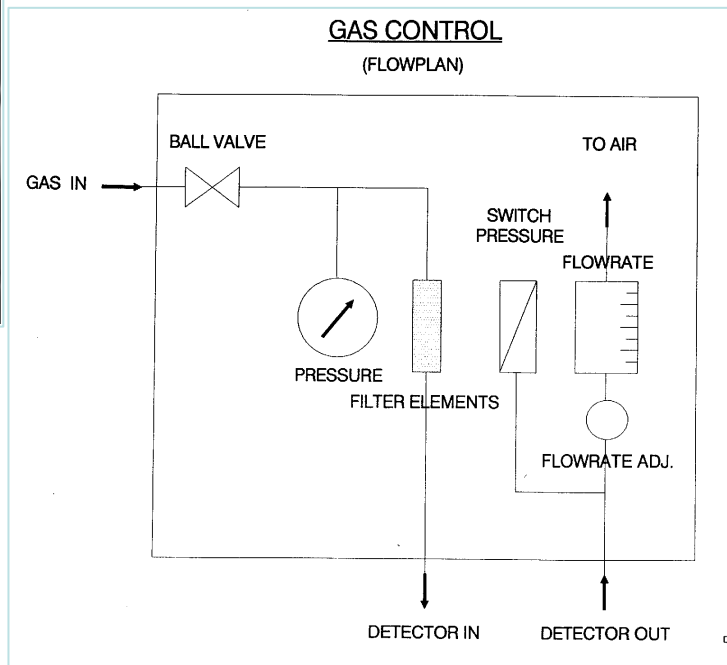
## 1D: Position Sensitive Detector

Argon (10% Methane) sau Xenon (10% Methane) intr-un sistem de curgere la presiune constanta.



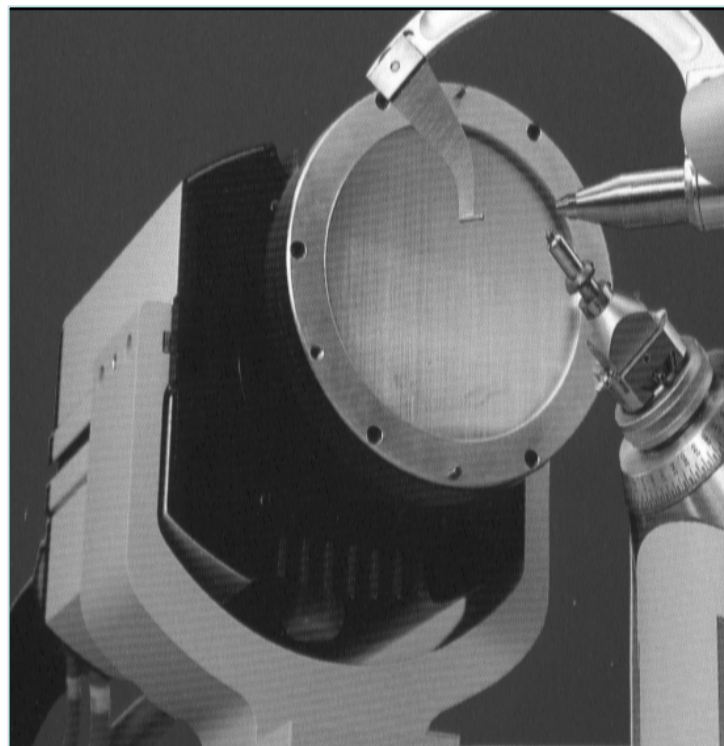
timp mort mic

Sol-X: detector cu semiconductor monocristal de Si ultrapur sau dopat

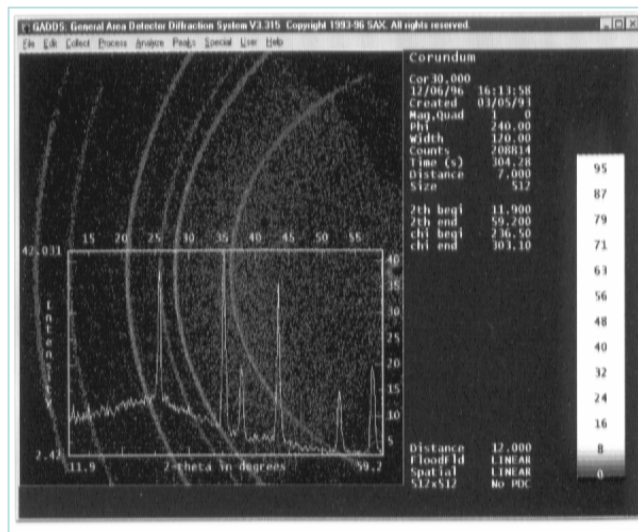
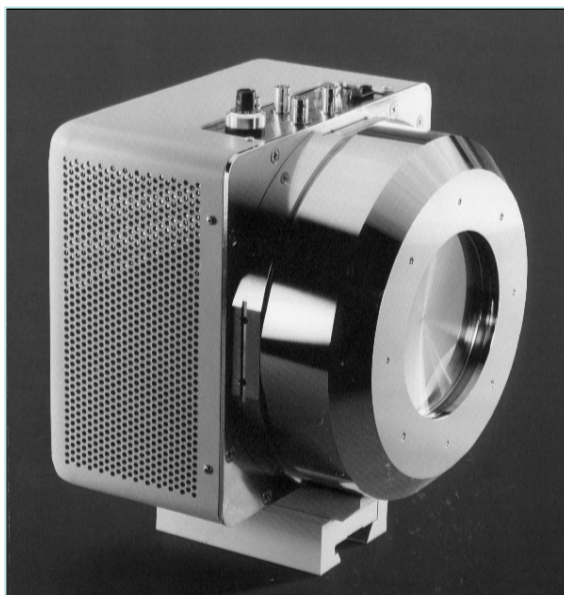


# D8 ADVANCE: Instrumentatie (7) Detectori

**2D HiStar**  
contor proportional multifire  
soft GADDS (parametri retea



**2D CCD**

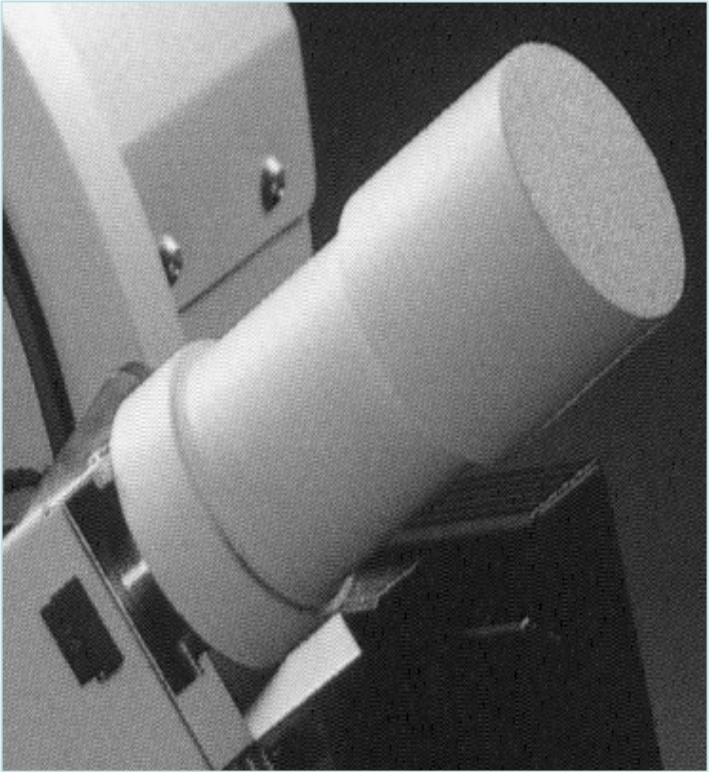
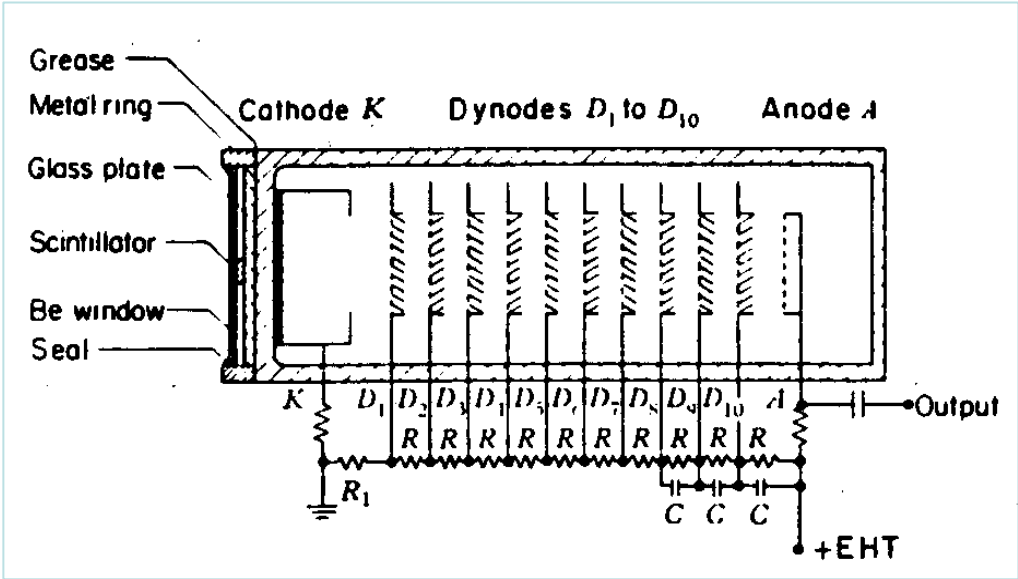


# D8 ADVANCE: Instrumentatie (8) Detectori

## Contor cu scintilatie

Model:

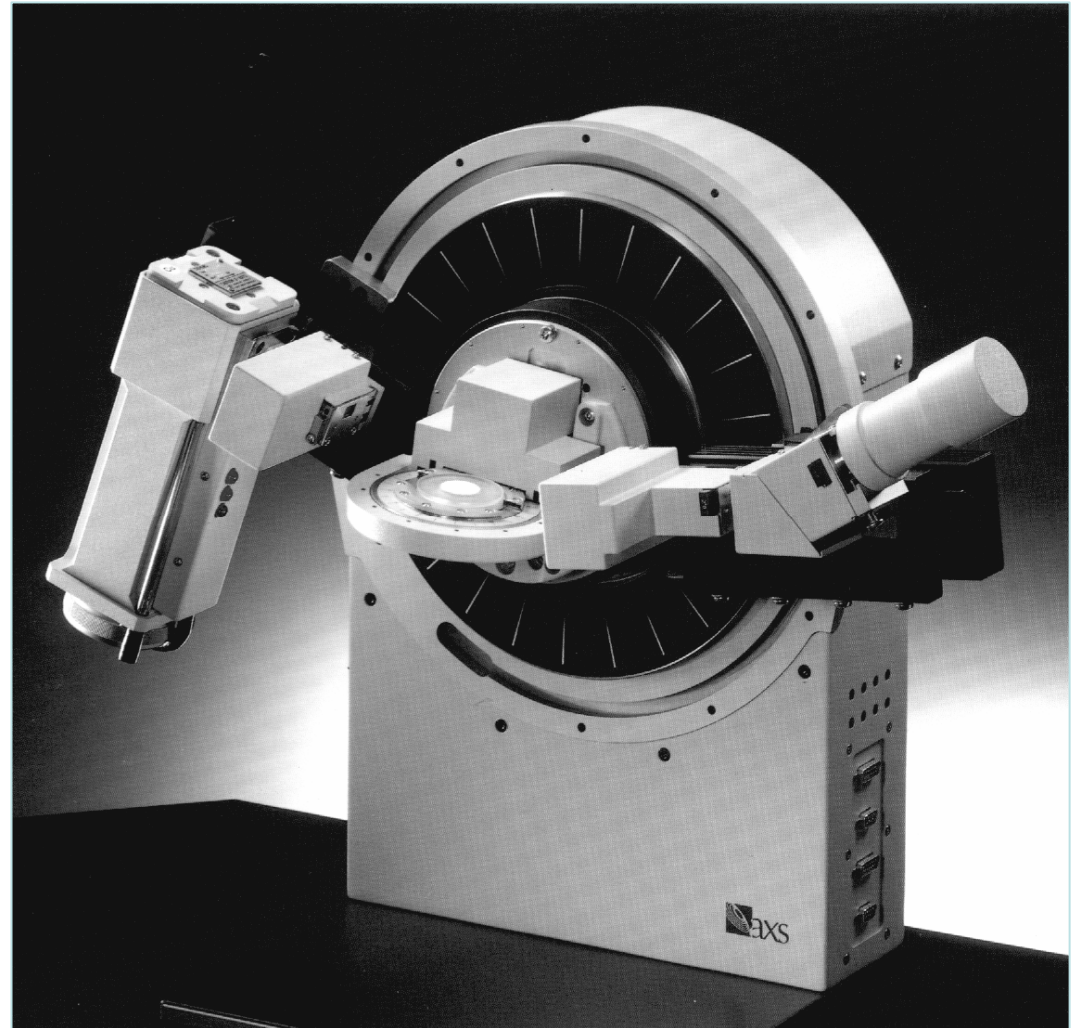
scintilator in UV + fotomultiplicator



## Metode de analiza (2)

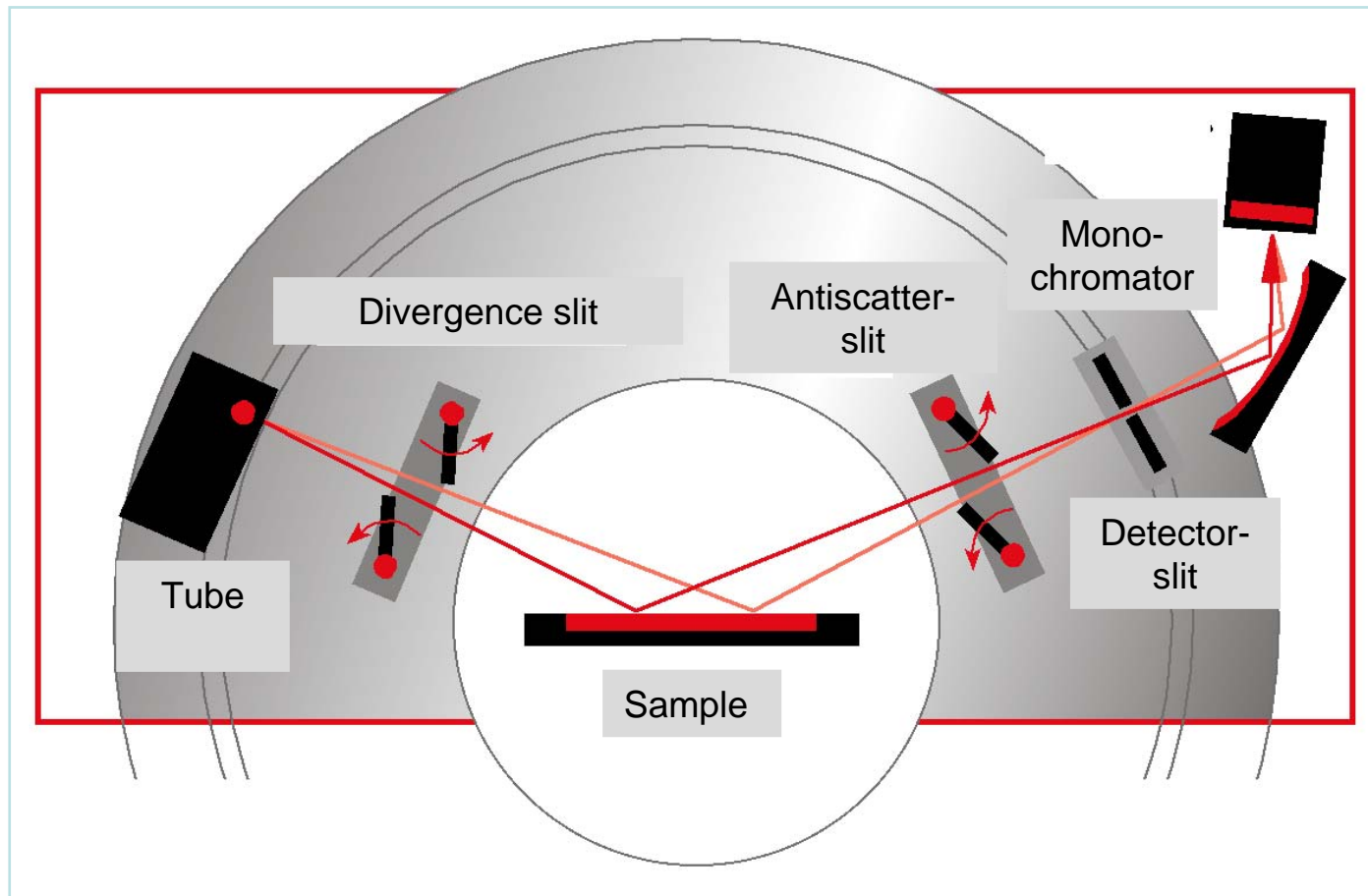
- Bragg-Bretano
- Fascicul Paralel: Oglinda Gobel
- Camera de temperatura
- Reflectometrie

cerc difractometric variabil



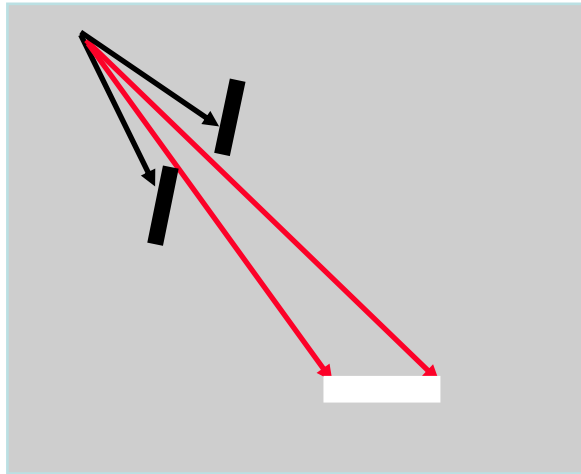
## Metode de analiza (3)

### Montaj Bragg-Brentano: principiu

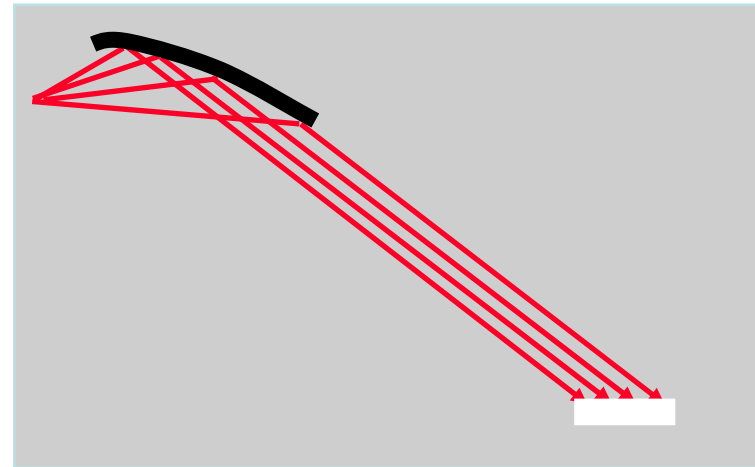


## Metode de analiza (4)

### Comparatie intre geometriile Bragg-Brentano si “paralel”



**Fascicul divergent**

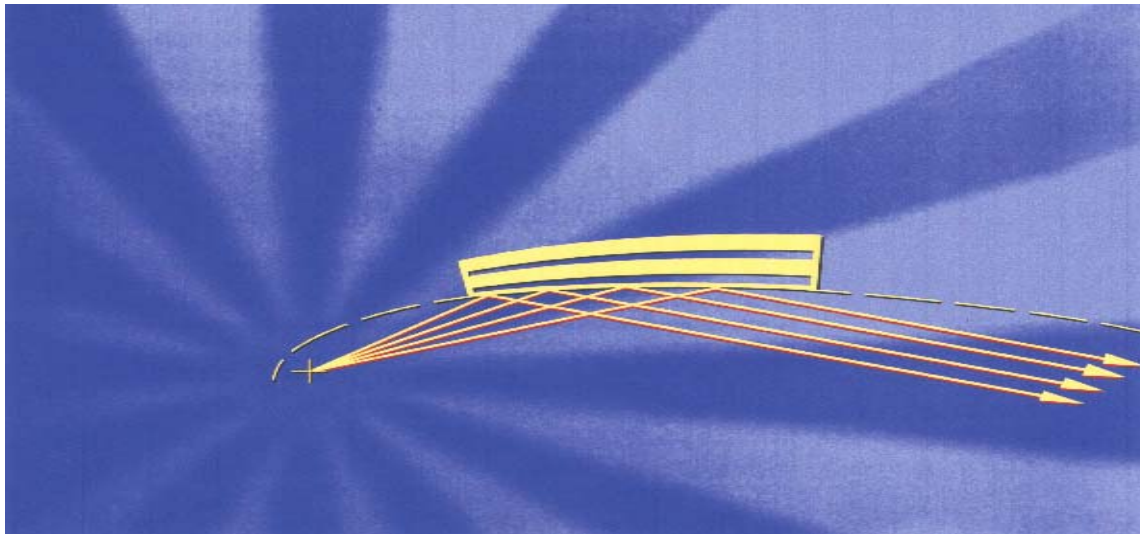


**Fascicul paralel**

## Metode de analiza (5)

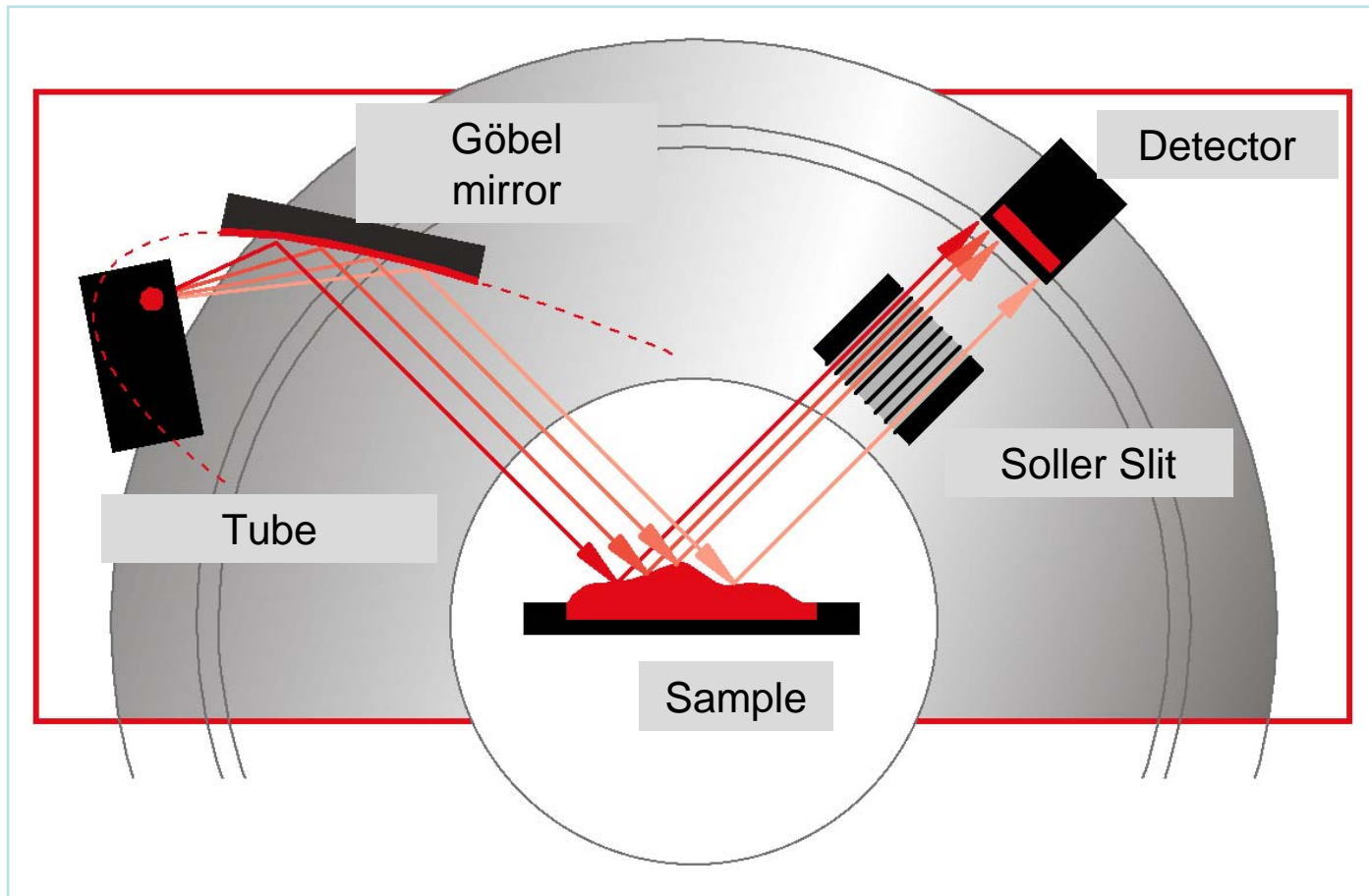
### Göbel Mirrors

- cristal curb multistrat
- capteaza radiatiile X de la sursa intr-un unghi solid larg
- produce un fascicul paralel si intens (!?) fara radiatii Cu  $K\beta$



## Metode de analiza (6)

### Principiul geometriei cu fascicul paralel (Göbel mirror)





## Metode de analiza (7)

### Posibilitati tehnice de inregistrare a datelor:

- ✓ **cercul difractometric: 150, 250 370 mm, independent**
- ✓ **miscare / stationare independenta a tubului si contorului**
- ✓ **auto-calibrare automata inaintea fiecarei probe**
- ✓ **pozitionare automata la unghiurile de plecare**
- ✓  **$2\theta$  minim =  $0,5^\circ$ ;  $2\theta$  maxim =  $160^\circ$  (functie de fante si proba)**
- ✓ **suportul de proba fix, orizontal**
- ✓ **tipul de inregistrare:  $0 \div 2\theta$ ,  $\theta \div \theta$ , Locked coupled scan, contor scan, tube scan**
- ✓ **precizie maxima de inregistrare:  $0,0001^\circ$  (cu limitari: temperatura, timp, suprafata, material, etc)**
- ✓ **ecartul pasului:  $0,001^\circ \div 1^\circ$**
- ✓ **viteza de inregistrare:  $0,01s \div 10 \text{ min} / \text{pas}$**
- ✓ **variante de inregistrare: continuu, pas cu pas**
- ✓ **autoscalarea numarului de impulsuri /s (intensitatea picului)**

## Metode de analiza (7): Camera de temperatura

**Model: MRI / TC-Wide Range**

- temperaturi de lucru: -170 °C (vid) / -150 °C (gaz inert ) ÷ 450 °C  
t camera ÷ 1200 °C
- termocuplu: K cromel/alumer, Pt-PtRh
- etaloane pentru: aliniere goniometru, temperatura
- mediul de lucru: aer, vid, gaz inert
- ferestre: kapron

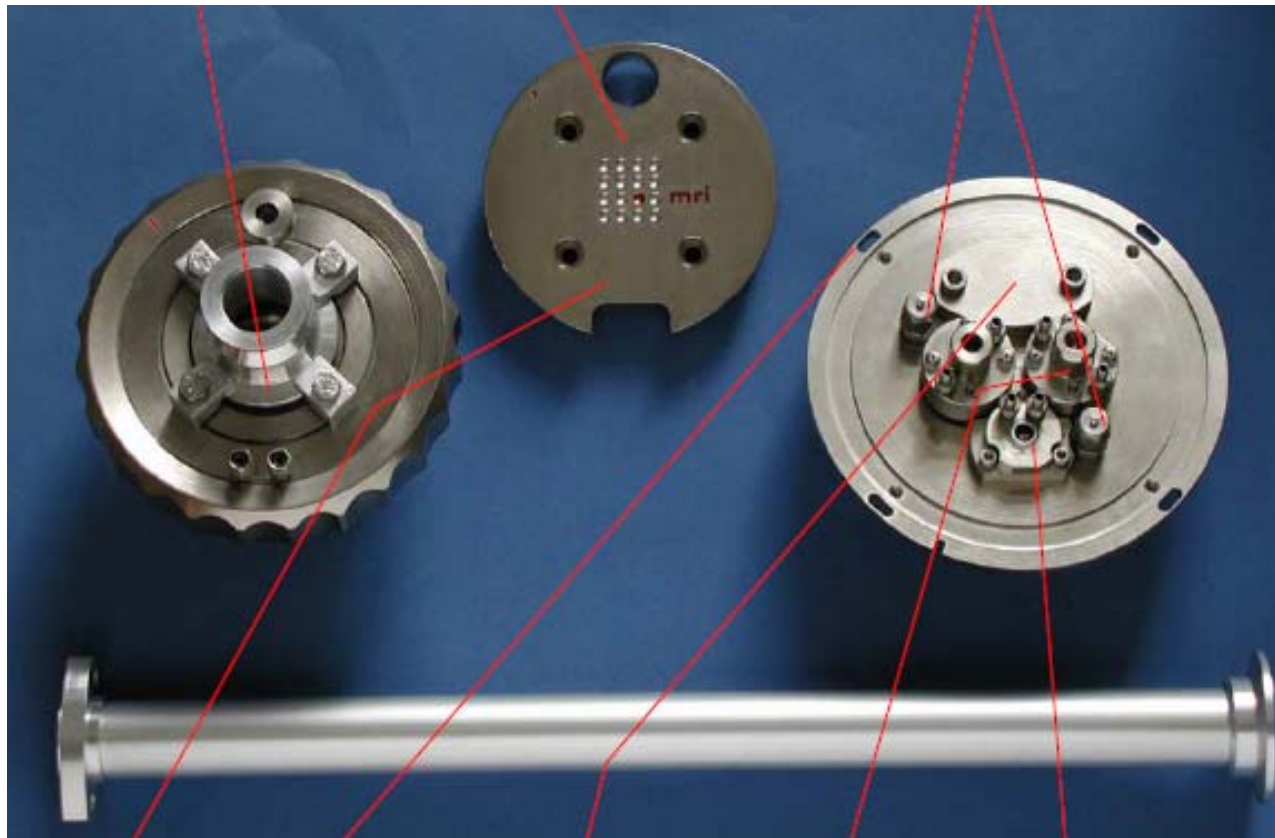
**Important!**

**Este montata o data la cateva luni**



## Metode de analiza (8): Camera de temperatura

- Accesorii:**
- pompa vid
  - vas Dewar azot lichid,
  - sistem racire / incalzire cu apa
  - sistem de vizualizare in interiorul camerei
  - joja si sistem de masurare a vidului,
  - controler si regulator de temperatura, cu precizie 1 °C , comandate manual sau prin soft
  - sisteme de protectie automata
  - posibilitatea de a programa “job-uri” pentru probe foarte lungi



## Metode de analiza (8): Camera de temperatura



**Suport proba: 10×10×0,7 mm**

**Probleme de aliniere in planul de zero:  
cu dilatari / contractii, cu topirea**



## Prepararea probelor (1):

### Intrebari:

- de ce este important de discutat de prepararea probelor?
- ce fel de metode de masurare de foloseste
- care sunt diferitele posibilitati de a prepara probele si avantajele diverselor metode?

## Prepararea probei este principalul motiv pentru erorile sistematice in difractometrie

### Principalele erori sunt::

- inaltimea probei: afecteaza valorile  $d$  – distantele interplanare si intensitatile picurilor  
⇒ rezultate eronate in analiza calitativa si cantitativa de faza, indexarea parametrilor retelei cristaline
- orientarea preferentiala (in cazul probelor cu aspect de ace sau foite): afecteaza intensitatea  
⇒ rezultate eronate in analiza calitativa si cantitativa de faza, prelucrarea Rietveld
- marimea nepotrivita a granulatiei: efecte de absorbtie, orientare preferata, probe neomogene  
⇒ rezultate eronate in analiza calitativa si cantitativa de faza, prelucrarea Rietveld
- compozitia granulometrica: poate distruge cristalinitatea  
⇒ rezultate eronate in analiza cantitativa de faza, prelucrarea Rietveld, determinarea dimensiunilor cristalitelor, grosimea picului la semi-inaltime

## Prepararea probelor (2):



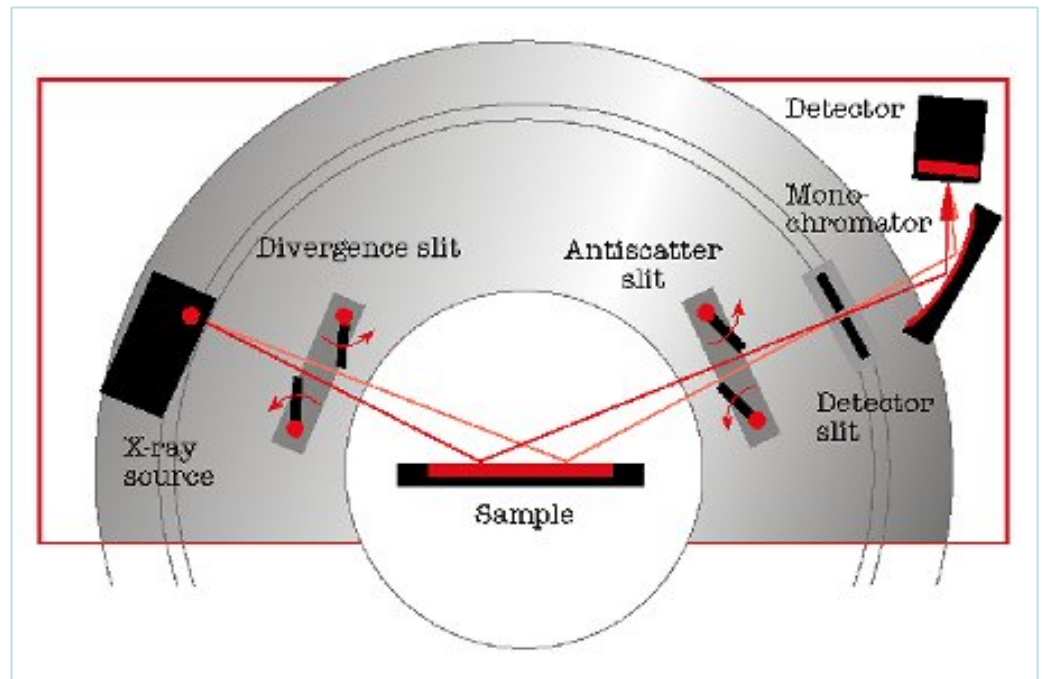
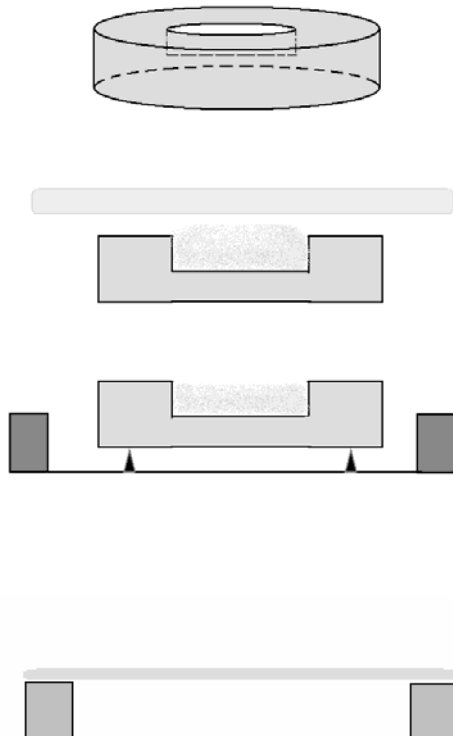
**IMPORTANT:** nu se consuma din material

### Tipuri de probe:

lichide, geluri

solide: pulberi, folii, placi cu o suprafata dreapta ( $\leq 30 \times 30$  mm)

fibre, fire



## Prepararea probelor (3):

### Suporturi de probe pentru montaj prin reflexie:

- prin fata suportului de proba
- prin spatele suportului
- prin lateral
- folosint suporturi de probe cu fond zero
- alte metode de preparare: presare, sprayere, scotch aditiv, etc.

#### Dimensiuni suporturi alama:

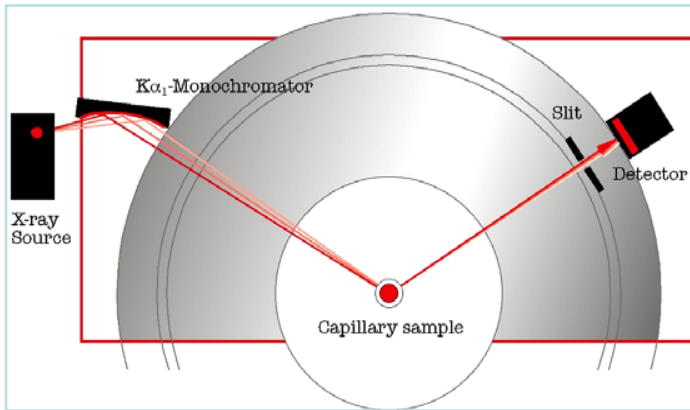
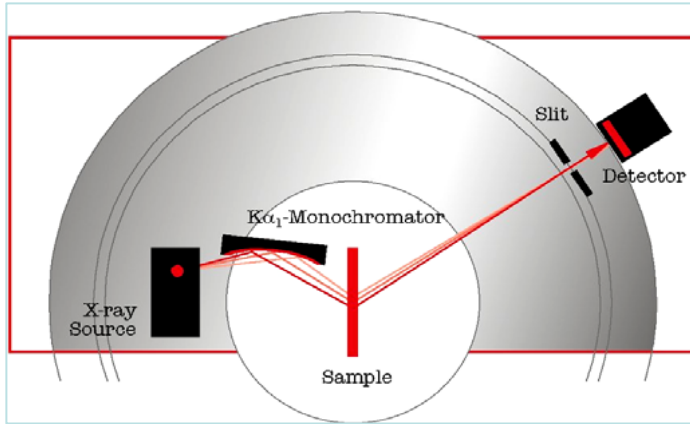
$\Phi$  25 mm  $\times$  0,5; 1,0; 2,0 mm

$\Phi$  15 mm  $\times$  0,5; 1,0; 2,0 mm

#### Dimensiuni pastila (matrita presa hidraulica 10 tf):

$\Phi$  11 mm  $\times$  0,5  $\div$  2,0 mm

## Prepararea probelor (4):

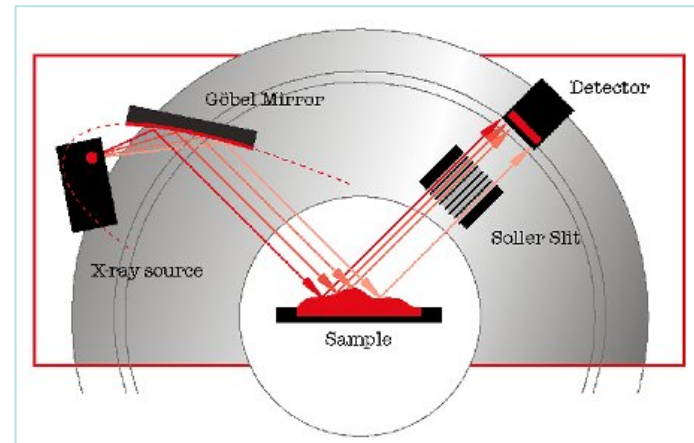


Suporturi de probe pentru montaj prin reflexie:

intre folii  
pe folii  
fibre

in capilare  
pe capilare  
pe fibre

**Oglinda Gobel:**  
probe denivelate, care nu pot fi distruse





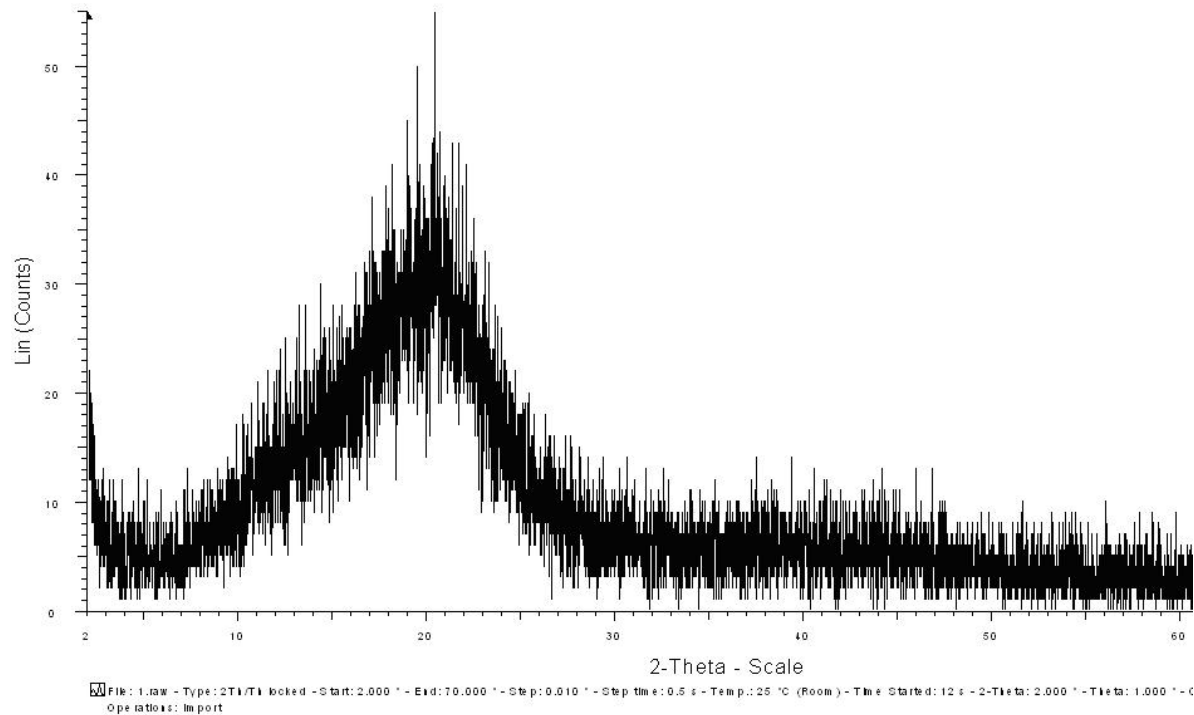
## Preluarea rezultatelor (1):

formate brute:

**fisier.raw**

**fisier.txt**

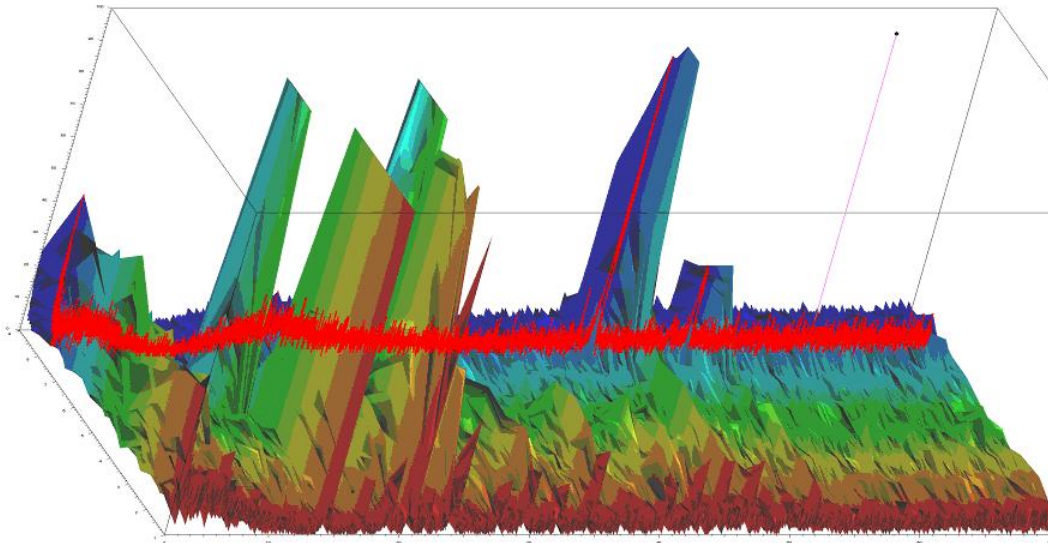
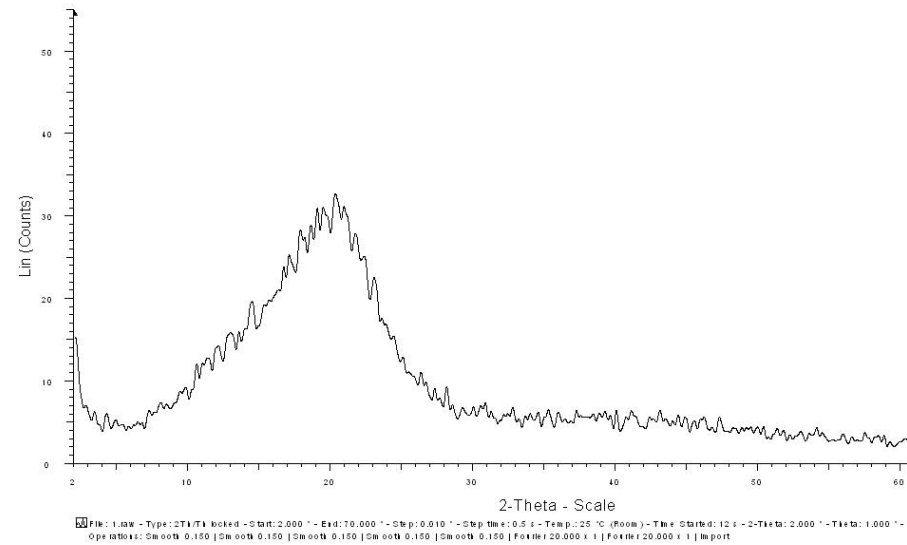
**fisier.wmf (32 bits)**

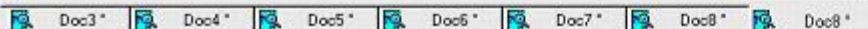
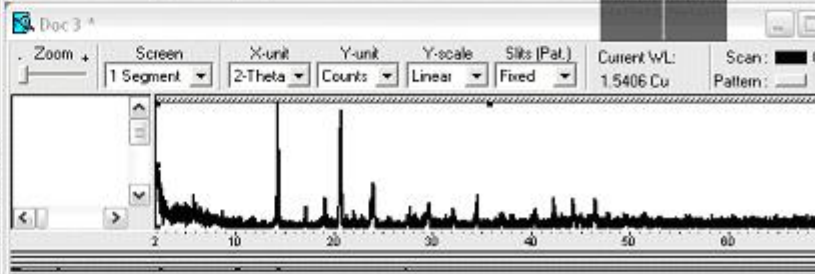
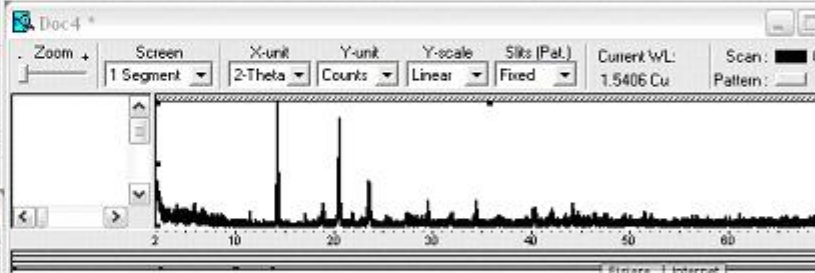
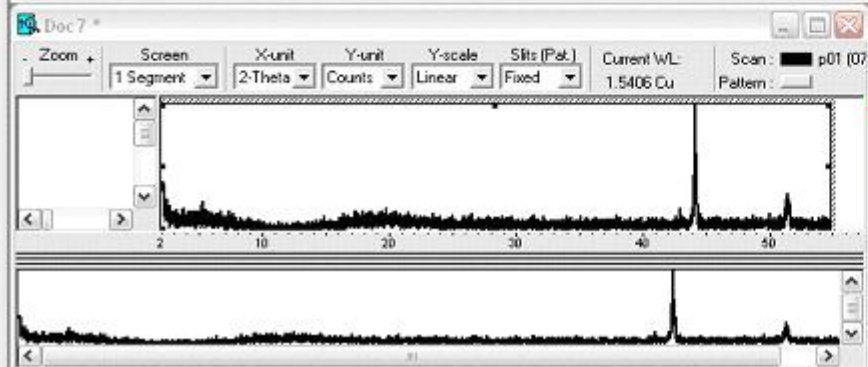
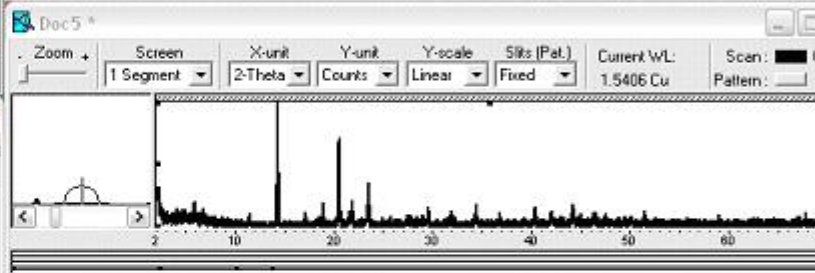
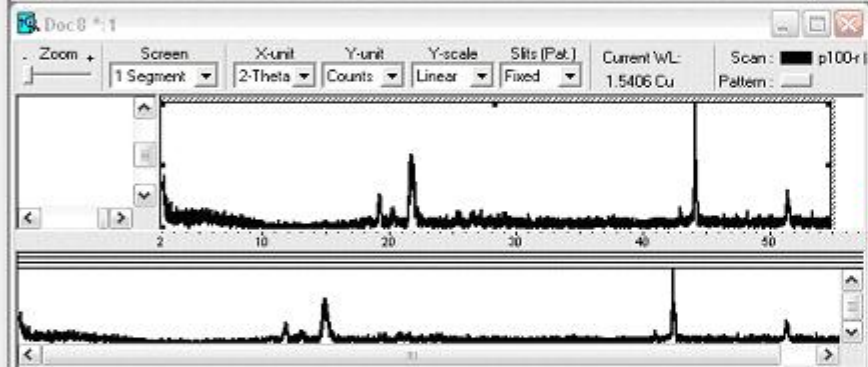
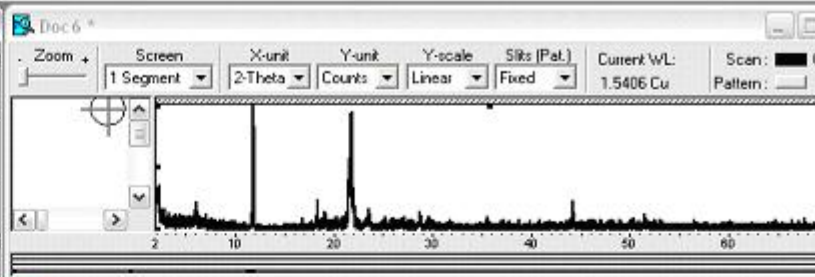
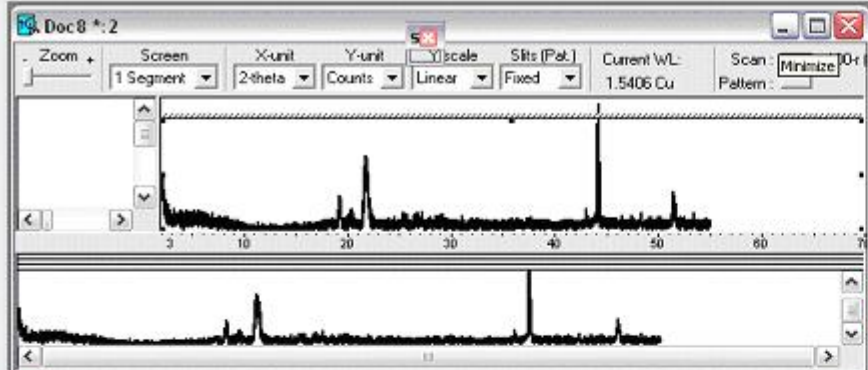


## Preluarea rezultatelor (2):

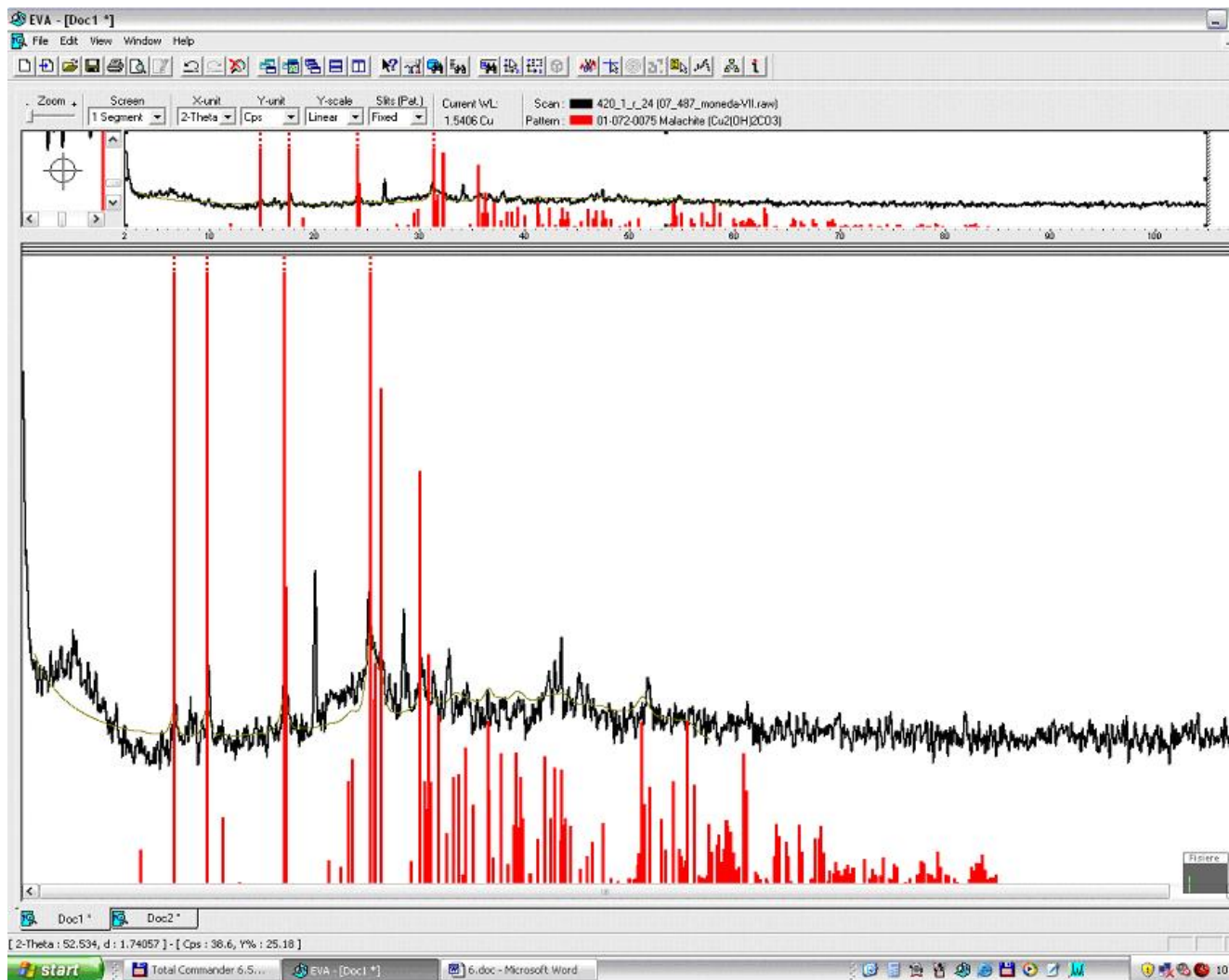
formate prelucrate:

difractograme multiple  
filtrari Fourier cu grade diferite  
fisiere Origin simple, multiple  
reprezentari grafice, filtrari diverse





## Preluarea rezultatelor (4):



# Preluarea rezultatelor (5):

Pattern: 01-072-0075		Radiation = 1.540600					Quality: Indexed				
Cu <sub>2</sub> (OH) <sub>2</sub> CO <sub>3</sub>		2 $\theta$	<i>i</i>	<i>h</i>	<i>k</i>	<i>l</i>	2 $\theta$	<i>i</i>	<i>h</i>	<i>k</i>	<i>l</i>
Copper Hydroxide Carbonate Malachite		11.967	31	1	1	0	53.155	5	2	5	1
		14.795	586	0	2	0	53.507	4	3	4	1
		17.553	708	1	2	0	53.682	5	3	5	-1
		18.893	61	2	0	0	53.905	17	5	3	0
		20.298	2	2	1	0	53.995	28	4	2	1
		24.067	690	2	2	0	54.225	148	1	6	-1
		24.209	272	1	3	0	54.225	148	4	4	-1
		27.838	32	0	0	1	54.481	73	1	7	0
		28.837	16	0	1	1	54.481	73	3	6	0
		28.468	94	3	1	0	54.913	89	5	2	-1
		29.823	114	0	4	0	55.186	59	1	6	1
		31.290	959	1	4	0	55.186	31	2	6	-1
		31.290	959	2	0	-1	55.574	94	4	3	1
		31.681	189	0	2	1	57.259	32	1	1	-2
		31.730	202	1	1	1	57.513	25	0	0	2
		32.200	453	2	1	-1	57.782	16	5	3	-1
		32.200	453	3	2	0	57.907	22	5	4	0
		34.340	1	1	2	1	57.907	22	2	4	-2
		34.779	21	2	2	-1	58.574	148	0	1	2
		35.536	377	2	4	0	58.562	91	3	5	1
		35.925	94	0	3	1	59.033	8	1	2	-2
		36.067	89	1	3	-1	59.330	6	4	5	-1
		36.250	210	2	0	1	59.408	5	2	6	1
		36.447	93	3	3	0	59.513	5	6	1	0
		37.045	154	2	1	1	59.735	8	0	2	2
		37.229	49	0	4	0	59.919	55	3	6	-1
		38.305	98	1	3	1	60.120	30	2	2	-2
		38.305	98	4	0	0	60.570	38	1	1	2
		38.774	100	2	3	-1	60.755	45	4	4	1
		38.774	100	1	5	0	60.873	20	4	6	0
		39.064	9	4	1	0	61.151	32	6	2	0
		39.346	125	2	2	1	61.241	68	0	7	1
		39.996	72	3	2	-1	61.341	58	5	1	1
		41.250	149	4	2	0	61.494	53	1	7	-1
		41.250	149	0	4	1	61.740	48	3	7	0
		41.376	86	1	4	-1	61.740	48	1	3	-2
		41.714	24	3	4	0	61.940	29	0	8	0
		42.332	119	2	5	0	62.191	13	1	2	2
		42.950	18	2	3	1	62.278	16	6	1	-1
		43.416	54	1	4	1	62.526	119	5	5	0
		43.556	120	3	3	-1	62.526	119	2	3	-2
		43.777	52	2	4	-1	63.048	85	1	7	1
		44.037	98	3	1	1	63.048	85	5	2	1
		44.191	60	4	0	-1	63.825	11	6	3	0
		44.747	10	4	3	0	63.972	9	6	2	-1
		44.888	10	4	1	-1	64.109	4	2	0	2
		45.410	41	0	6	0	64.224	5	2	1	2
		46.040	117	3	2	1	64.541	3	1	3	2
		46.483	50	1	6	0	65.389	25	2	8	0
		46.850	166	4	2	-1	65.583	55	5	3	1
		47.303	40	0	5	1	65.583	55	3	3	-2
		47.476	105	1	5	-1	65.821	44	4	1	-2
		47.823	54	2	4	1	66.359	38	2	7	1
		47.780	80	3	5	0	66.359	38	5	5	-1
		48.182	53	3	4	-1	66.492	25	6	3	-1
		48.654	14	5	1	0	66.492	25	2	4	-2
		49.593	25	2	5	-1	66.820	3	3	7	-1
		49.593	25	2	6	0	67.469	54	6	4	0
		50.020	38	4	3	-1	67.710	30	4	7	0
		50.912	56	5	2	0	68.467	4	1	4	2
		51.613	5	4	0	1	68.553	5	5	6	0
		52.216	3	4	1	1	68.853	43	2	3	1
		53.165	5	5	1	-1	69.180	42	0	6	0

## **DIFFRAC<sup>plus</sup> software: (existente)**

- calculator de proces:
- achizitie date: **DIFFRAC<sup>plus</sup> Basis:**
- evaluare date: **DIFFRAC<sup>plus</sup> Evaluation: EVA, AbsorbX, D8Viewer, Dquant, FileExchange, RawFileExchange**
- baza de date: **PDF-2 (format rdb)**
- prelucrare date: **TOPAZ P, TOPAZ N, TOPAZ I,**
- reflectometrie: **LEPTOS**