

IAEA virtual training on measurement techniques for natural and artificial radionuclides and radiochemical methods for their determination in marine environment

11 October 2021 - 12 November 2021

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MALAYSIA



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Atoms for Peace and Development

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Session 42. **Determination of C-14 in natural samples**

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MYA7008-2104243

MYANMAR

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- Absorption of CO_2 – LSC-a

- Validation of LSC-A and LSC-B

Counting

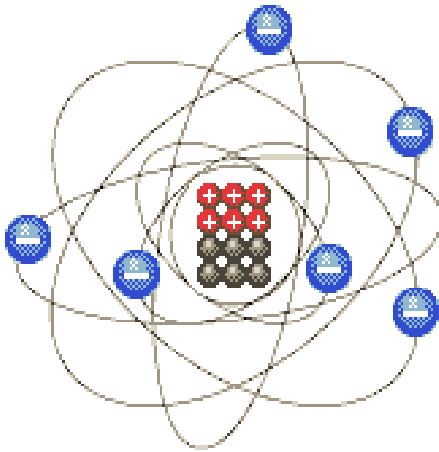
Quality control

Application of LSC techniques – monitoring

AMS

Biogenic component

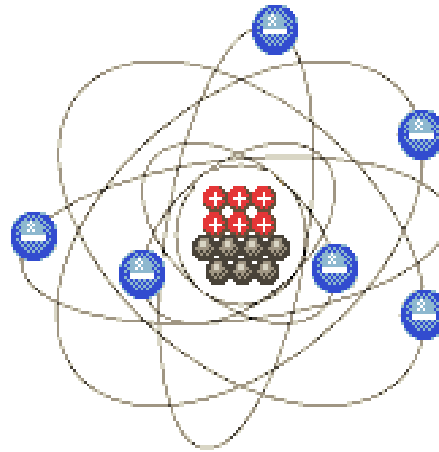
Carbon isotopes



^{12}C

98.89 %

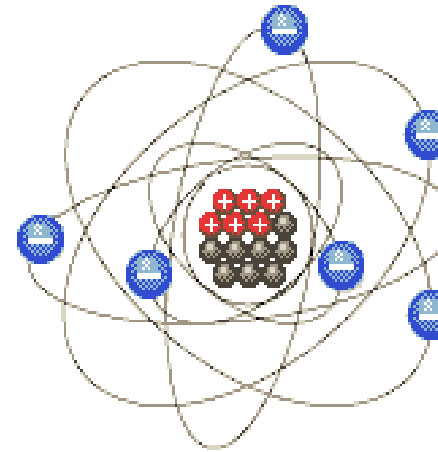
$p = n = 6$



^{13}C

1.11 %

$n = 7$



^{14}C

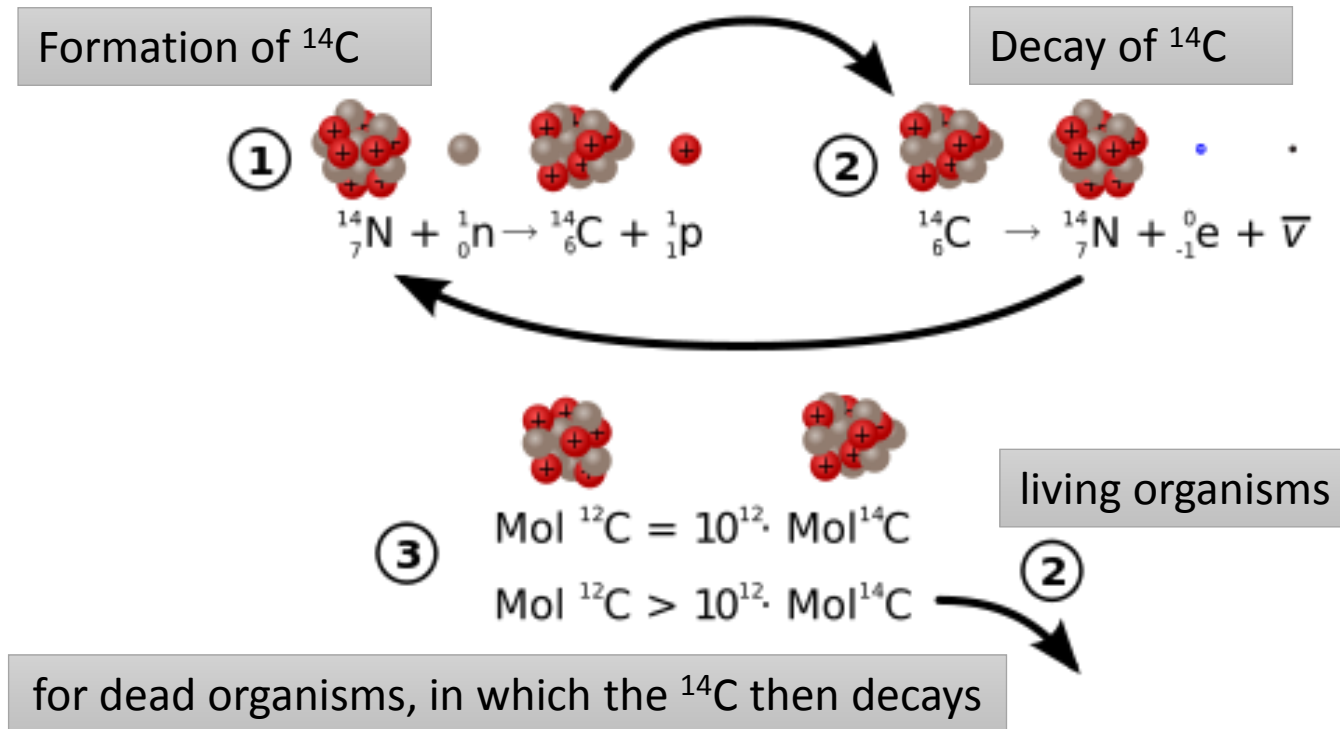
10^{-10} %

$n = 8$

$T_{1/2} = 5730 \text{ y}$

Radiocarbon production

Cosmogenic radionuclide - the primary natural source of ^{14}C on Earth is nuclear reaction between neutrons from cosmic rays with nitrogen in the atmosphere (The highest rate of ^{14}C production takes place at altitudes of 9 to 15 km)



Discovery of ^{14}C

The American scientist Professor Martin Kamen was the co-discoverer of the radioactive isotope carbon-14. The finding transformed biochemistry as a tracer following chemical processes in plants, while its use in the carbon dating of fossils and ancient artefacts between 500 and 50,000 years old revolutionized archaeology.

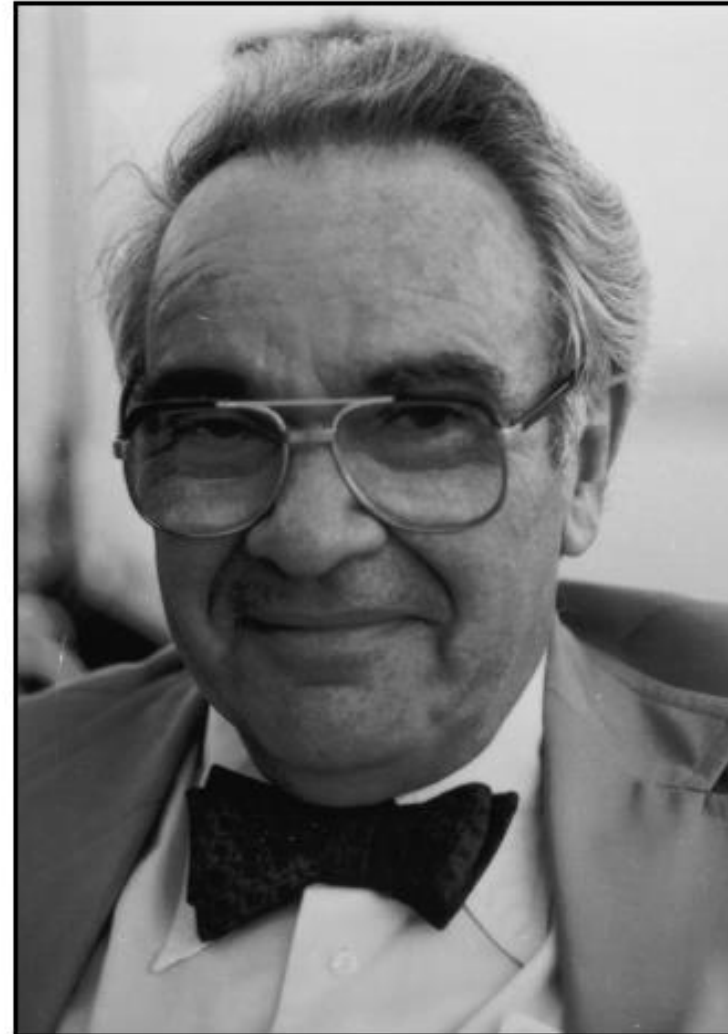
Obituary

Martin Kamen

Scientist, co-discoverer of the isotope that gave archaeology carbon-dating, and innocent victim of America's Communist witchhunts

(Pearce Wright , [The Guardian](#),
Monday 9 September 2002)

MARTIN DAVID KAMEN



27 AUGUST 1913 · 31 AUGUST 2002

Science 10 May 1963:
Vol. 140 no. 3567 pp. 584-590
DOI: 10.1126/science.140.3567.584

Sam Ruben and Martin Kamen co-discovered the isotope carbon-14 on February 27, 1940, at the University of California Radiation Laboratory, Berkeley, when they bombarded graphite in the cyclotron in hopes of producing a radioactive isotope of carbon that could be used as a tracer in investigating chemical reactions in photosynthesis. Their experiment resulted in production of carbon-14.

Ruben S, Kamen MD (1940)
Radioactive carbon of long-half life.
Phys. Rev. 57: 549

Martin Kamen, has been named one of two winners of this year's (1995) Enrico Fermi Award. The 82-year old Kamen is joined by 83-year-old physicist Ugo Fano, who won for his pioneering contributions to the theory of atomic and radiation physics.

Early History of Carbon-14

Discovery of this supremely important tracer was expected in the physical sense but not in the chemical sense.

Martin D. Kamen

When, how, and why was carbon-14 discovered? As T. S. Kuhn has remarked (1), discovery is seldom a single event that can be attributed wholly to a particular individual, time, or place. He notes that some discoveries, such as those of the neutrino, radio waves, and missing isotopes or elements, are predictable and present few problems, as far as establishment of priority is concerned. Others, such as the discoveries of oxygen, x-rays, and the electron, are unpredictable. These put the historian in a "bind" when he tries to decide when, how, who, and where the discovery was made. Much more rarely does he have a basis for an answer to the question "Why?"

I propose in this account of the "prenatal" history of carbon-14 to provide the answers to my leading questions (2). These make a story which is a fragment of the whole record. That record must be constructed by future historians who seek to probe the events of a period in which there has been an unparalleled impact of intellectual curiosity and scientific creativity on the structure of society.

The tremendous outburst of technology in the past half century, the result of the rise of nuclear science, has crowned man's quest for the philosopher's stone so successfully as to be hardly credible even to the most optimistic alchemist. Tracer methodology, an offspring of nuclear science, has provided essential support for the everwidening and deepening knowledge of structure and function in biological systems, expressed as the dynamic science of molecular biology.

These developments have profound, but unknown, implications for the future of our social structures. They obviously bring with them an unexampled load of grist for the mills of cultural historians, social scientists,

and philosophers. Perhaps the novelists will dig into the record of these exciting times for fresh insights into the age-old drives of mankind.

Carbon-14, the long-lived carbon isotope, is the most important single tool made available by tracer methodology, because carbon occupies the central position in the chemistry of biological systems. Thus it plays, and will continue to play, an essential role in the elucidation of biochemical mechanisms, knowledge of which is essential in the further development of molecular biology. Obviously, the circumstances surrounding its discovery are valid objects of interest for the historian (3).

Initial Phases, 1934-36

In the early 1930's, nuclear physics, immersed in the great traditions of the Cambridge school led by Ernest Rutherford, was concerned primarily with observations of processes associated with the scattering of elementary nuclear particles by various atomic nuclei. Reports in those times show painstaking determinations of range-energy relations for the fundamental projectiles (protons, deuterons, alpha particles). The energies used did not exceed approximately 10 Mev, because of the limitations set by the relatively primitive accelerators and by the radiation characteristics of the naturally radioactive materials that were available. The rationale for such work, which often involved tedious attention to detail and much labor, was that if enough precise facts were put together, accurate binding energies for nuclei could be deduced. From these energies, it was reasoned, there could be derived a solid basis for further attack on the problem of the nature of nuclear forces.

By 1933, such data—binding energies, angular distributions in scattering experiments, and so on—had demonstrated that nuclear forces could be described as analogous to saturation exchange forces like those postulated previously for chemical bonding. The so-called "alpha-particle" model of the nucleus already contained the seeds of what was to be the full-fledged modern "shell" theory of nuclei, to be developed later by Maria Mayer, Eugene Feenberg, and others.

As to my part in this, I was a young, eager student and had just begun doctoral research, using the Wilson cloud chamber to study the angular distribution of neutrons scattered in collisions with protons and other nuclei. These researches were part of a general program initiated in the laboratory of W. D. Harkins in the chemistry department at the University of Chicago (4). My decision to work in this field was largely a result of the influence of D. M. Gans, Harkins' associate and an assistant professor in the department (5).

Most significantly for this history, similar work was also under way at Yale, where F. N. D. Kurie, investigating neutron-induced disintegration of light elements, had obtained certain anomalous results for the angular distributions of protons in collisions with neutrons. In 1934 he proposed a radical interpretation (6) of certain events he noted in the cloud chamber. When nitrogen was exposed to fast neutrons, for instance, he noted that in some cases the ejected nucleus produced a very long, thin track. This he ascribed to a proton, rather than to an alpha particle. Thus, he supposed that the usual reaction, $N^{14}(n,He)^{11}B$, was accompanied by a less frequent but readily observable reaction, $N^{14}(n,H)^{14}C$. (As far as I am aware, this is the first suggestion in the literature that C^{14} might exist.) Kurie also suggested, however, that the tracks he was observing might arise from H^1 , or even H^2 , and thus that the reactions $N^{14}(n,H^2)^{15}C$ and $N^{14}(n,H)^{14}C$ were also possibilities. In fact, he felt the reactions with emission of H^1 and H^2 were the more likely because they resulted in nuclei of known stability.

The author is professor of chemistry at the School of Science and Engineering, University of California, San Diego. This article is adapted from a paper which he presented at a meeting of the American Chemical Society in Los Angeles in April 1963, when he received the Society's 1963 Award for Nuclear Applications in Chemistry. This paper is also being printed in the May issue of the *Journal of Chemical Education*.

After discovery of radioactive carbon-14, Ruben and Kamen found that it had a half-life of about 5,700 years and that some of the nitrogen in the atmosphere was turned into carbon-14 when hit with cosmic rays. Thus, an equilibrium was reached, the newly formed carbon-14 replacing the carbon-14 that decayed, so that there was always a small amount in the atmosphere.

[Ruben S, Kamen MD \(1940\) Radioactive carbon of long-half life. Phys. Rev. 57: 549](#)

Ruben and Kamen had to abandon attempts to experiment with ^{14}C in 1942.

Willard Libby, a chemist at the University of Chicago, experimented with carbon-14 further. He figured that plants would absorb some of this trace carbon-14 while they absorbed ordinary carbon in photosynthesis. Once the plant died, it couldn't absorb any more carbon of any kind, and the carbon-14 it contained would decay at its usual rate without being replaced. **By finding the concentration of carbon-14 left in the remains of a plant, you could calculate the amount of time since the plant had died.** He continued to refine the concept for the next decade, calculating the age of an ancient Egyptian barge using wood samples. The science of archaeology was revolutionized and, for his efforts, Libby received the Nobel Prize in Chemistry for 1960.

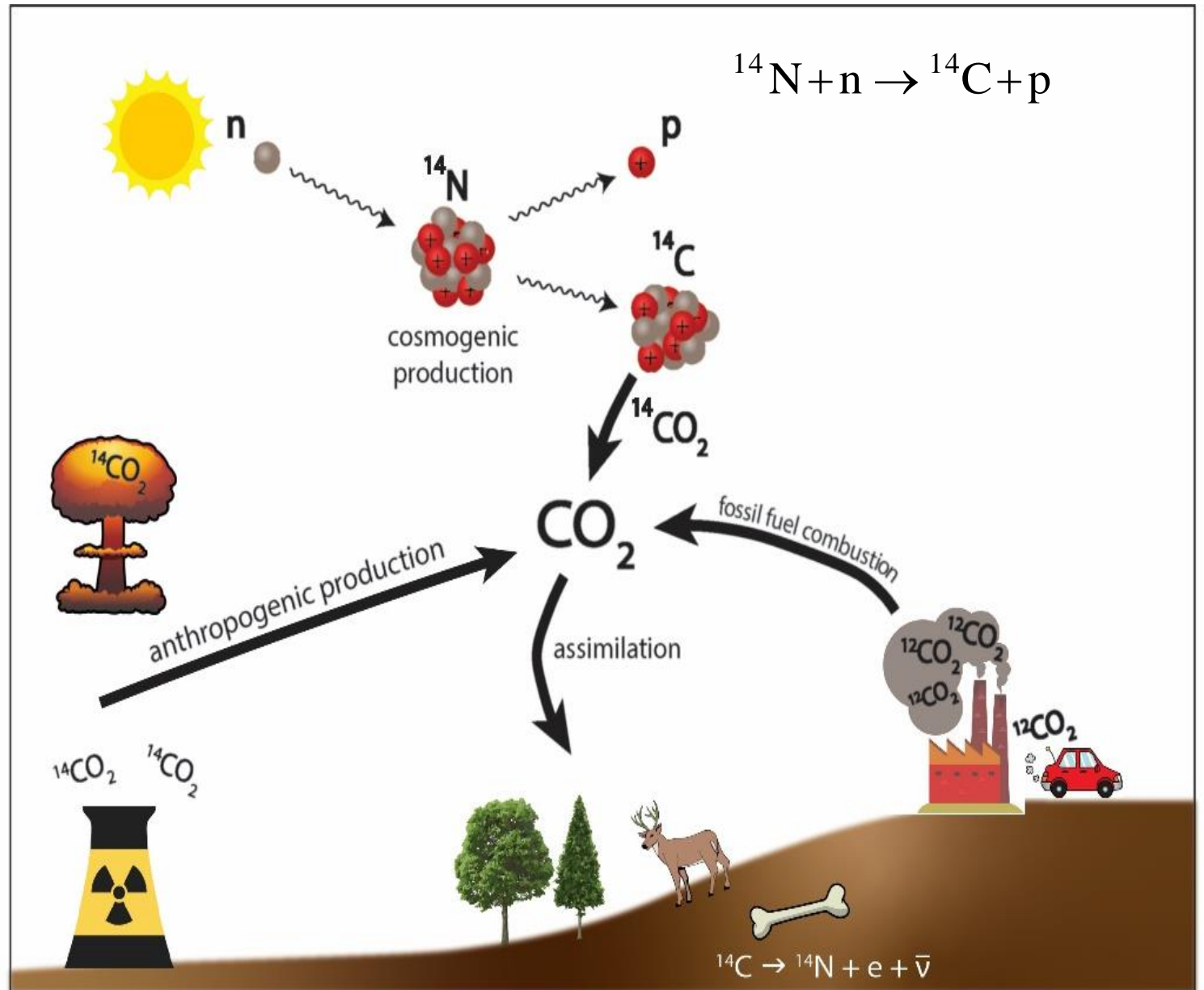
¹⁴C

Radiocarbon is of both cosmogenic and anthropogenic origin.

- **Cosmogenic** or natural radiocarbon is formed in the atmosphere in nuclear reactions
- **Anthropogenic** carbon is produced in (1) various nuclear facilities and (2) during atmospheric nuclear and thermonuclear bomb testing.
- Anthropogenic source of carbon (¹⁴C-free) – use of fossil fuels for energy production

Krajcar Bronić, I. et al. (2020)

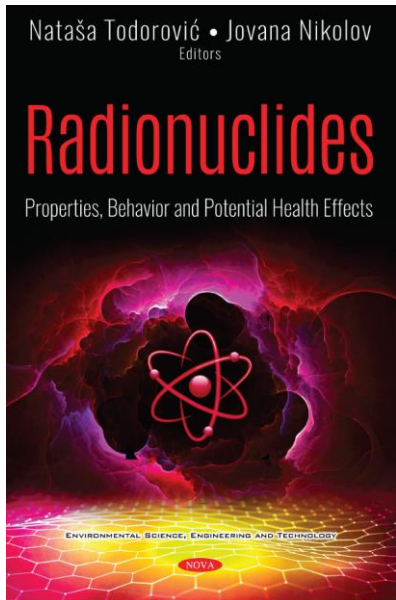
[Properties, behavior and potential health effects of ¹⁴C..](#)



After formation, ^{14}C is almost immediately oxidized to CO_2 and then together with other carbon isotopes enters the biological and geochemical carbon cycles. In the photosynthesis process, it becomes part of the biota and thus enters the food chain. In such a way, a uniform and equilibrium distribution of ^{14}C in the atmosphere and biosphere is attained.

Radiocarbon behaves in the same way as other carbon isotopes in the environment and in the body. The specific activity of ^{14}C is the same in terrestrial plants as in the atmospheric CO_2 used for photosynthesis.

Carbon, including ^{14}C , is thus a constituent of food and contributes to the natural irradiation of man through the food chain, and if the ^{14}C activity is higher than the natural one, it may cause the increase of the effective dose to population.



QUANTITIES AND UNITS SPECIFIC FOR ^{14}C

There are several conventions for expression of radiocarbon activities.

Basic quantity is specific activity $A^{14}\text{C}$, i.e., activity per unit mass of carbon, Bq/kgC.

However, more common unit is relative specific activity $a^{14}\text{C}$,

$$a^{14}\text{C} = \frac{A^{14}\text{C}}{A_{\text{ref}}^{14}\text{C}}$$

$A_{\text{ref}}^{14}\text{C}$ is the specific activity of a referent material from AD 1950
(AD = Anno Domini) equal to 226 Bq/kgC

The value of $a^{14}\text{C}$ for natural samples (before AD 1950, i.e., before anthropogenic disturbances) lies between 0 and 1. Recently, a new name of the quantity has been introduced: $F^{14}\text{C}$ (fraction modern carbon), $a^{14}\text{C} = F^{14}\text{C}$, and their values are <1 for old samples (before AD 1950) and usually >1 for recent samples from “bomb period” or post-bomb

$a^{14}\text{C}$ – it is expressed as percentage of modern carbon, and such “unit” is called pMC – percent of modern carbon

$$a^{14}\text{C} = 100 \text{ pMC}$$

$$F^{14}\text{C} = 1$$

$$A^{14}\text{C} = 226 \text{ Bq/kgC}$$

All these values are equivalent

Isotopic fractionation

- Isotopic fractionation is defined as the relative partitioning of the heavier and lighter isotopes between two coexisting phases in a natural system - various physical and chemical processes are mass dependent and thus they cause isotopic fractionation
- Usually, the ratio of the heavier, less abundant, isotope to the lighter, most abundant, isotope ($^{13}\text{C}/^{12}\text{C}$) is compared in various compounds

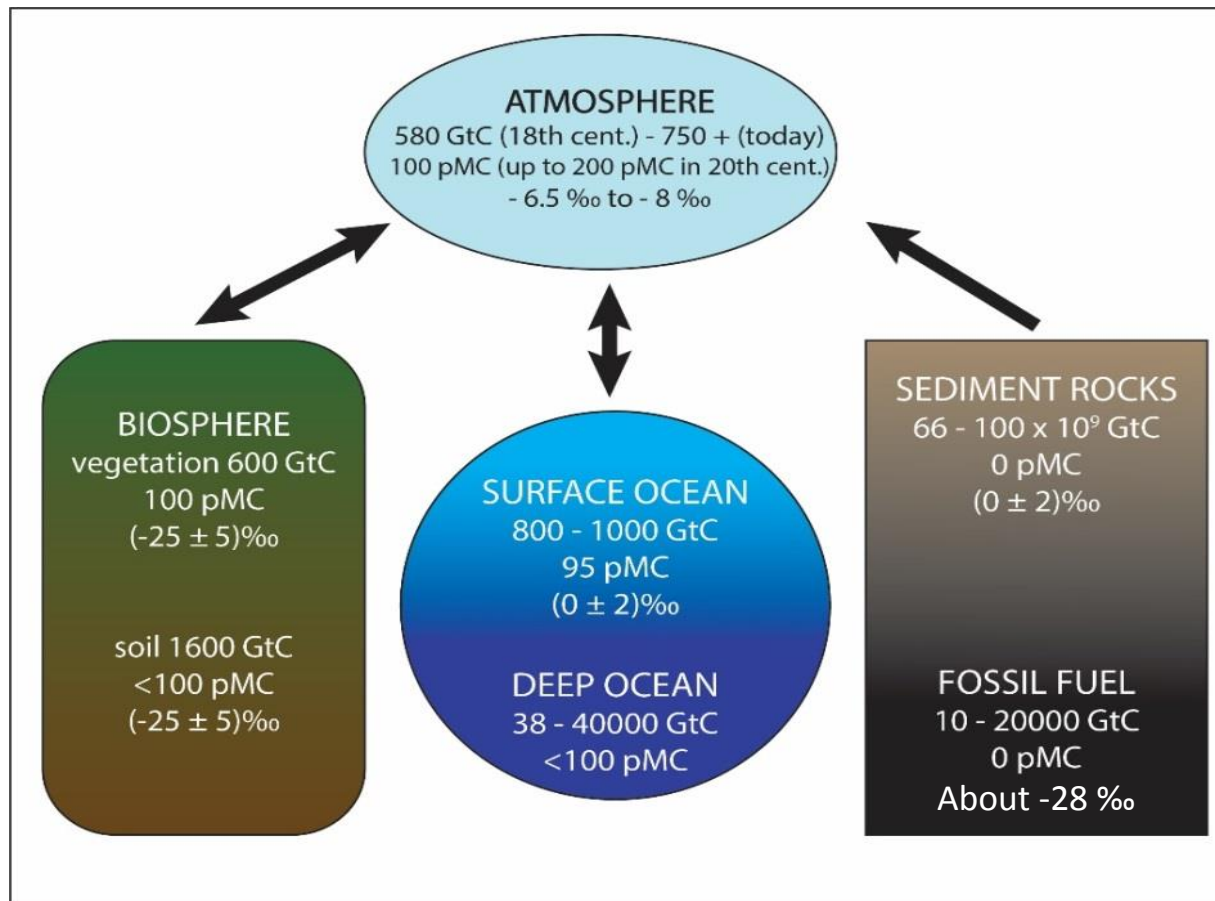
$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \quad R = ^{13}\text{C}/^{12}\text{C}$$

the quantity δ as the relative difference, expressed in ‰, of the ratio R in a sample and R in the standard
The international standard for $\delta^{13}\text{C}$ is VPDB (Vienna PDB, for Pee Dee Belemnite)

The δ value is usually small, and therefore it is expressed in ‰.

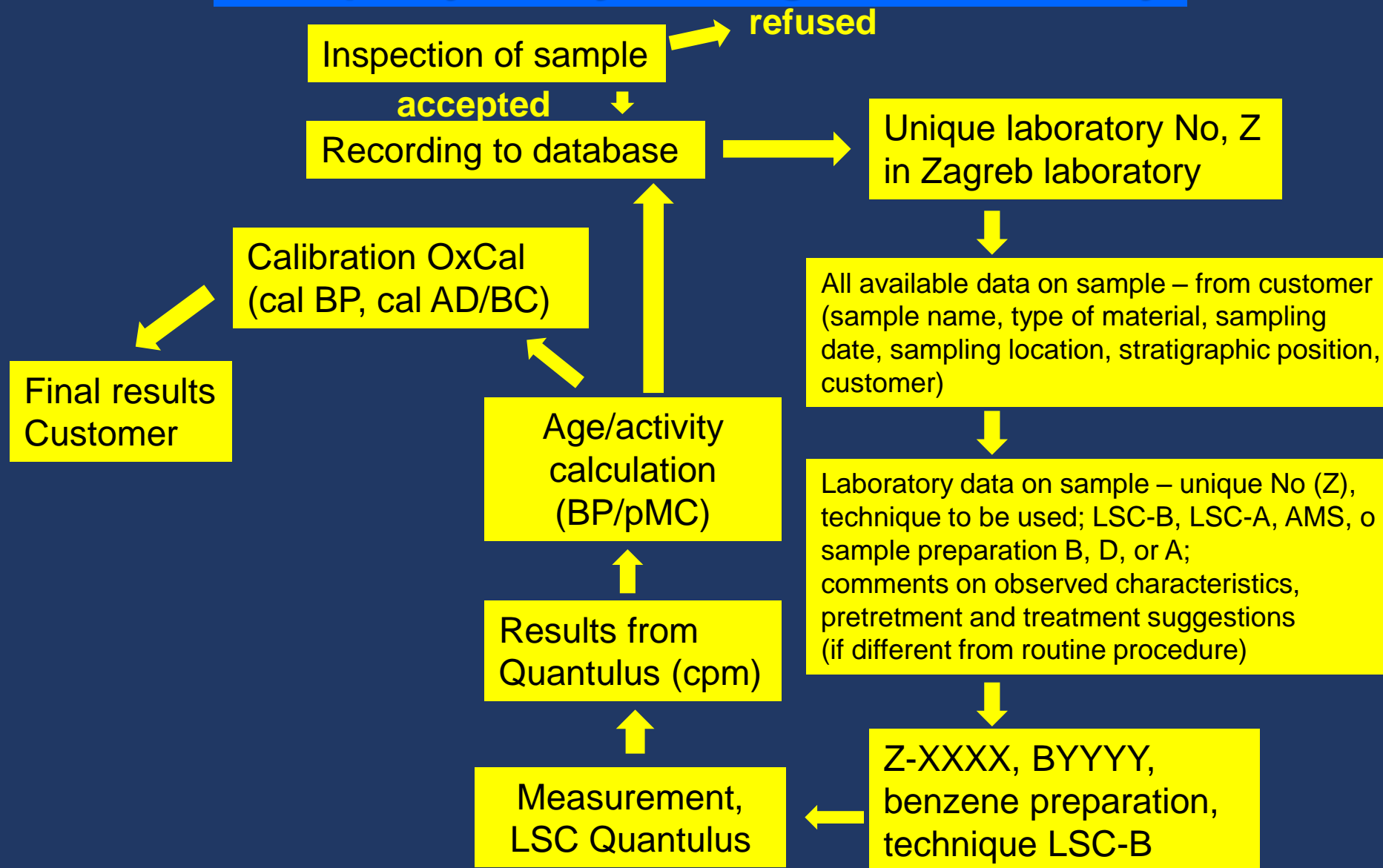
Isotope fractionation occurs to both ^{13}C and ^{14}C , and the fractionation for ^{14}C is known to be about twice that for ^{13}C , the $\delta^{13}\text{C}$ value of the sample material can be used for fractionation correction of the measured ^{14}C activities.

It has become common practice to normalize ^{14}C results to the value $\delta^{13}\text{C} = -25 \text{ ‰}$



Schematic presentation of carbon reservoirs that take part in carbon cycle. For each reservoir the following values are given: carbon inventory in GtC (Gigatone carbon), relative specific activity $a^{14}\text{C}$ in pMC, and $\delta^{13}\text{C}$ in ‰.

Sample „journey” through the laboratory



Inspection of the sample

Submitted sample (by submitter):

Washed and cleaned – removing of *in situ* contaminations, i.e., plant remains, leaves, roots (modern)

Dry and properly packed – inert material

Properly marked – sampling site, sampling date, sample ID

**Good sample – without un-removable contaminants (impregnation)
 big enough
 related to the investigated event**

Acceptance of the sample → assigning unique laboratory No (Z in Zagreb)

Recording to database

Plus all sample information from submitter which submitter knows / can / wish to share with laboratory (sometimes is one letter or one number the only information on a sample)

Sample types

Organic: leaves, wood, seeds, sediments, soil, textile, paper,

Carbonate: shells, speleothems, tufa, travertine, lake sediments, corals

Bones: collagen (organic), cremated (carbonate) [AMS!]

Dissolved: organic (DOC) and inorganic (DIC)

Gaseous: CO₂, CH₄, CO and hydrocarbons in air and soil

biomedical tracers [AMS!]



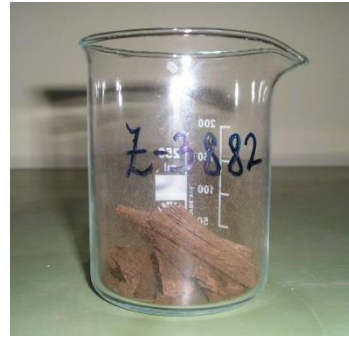
Bone



Bone collagen



Wood



Pretreated wood



Carbonised
wood



Speleothem



Charcoal
with dirt

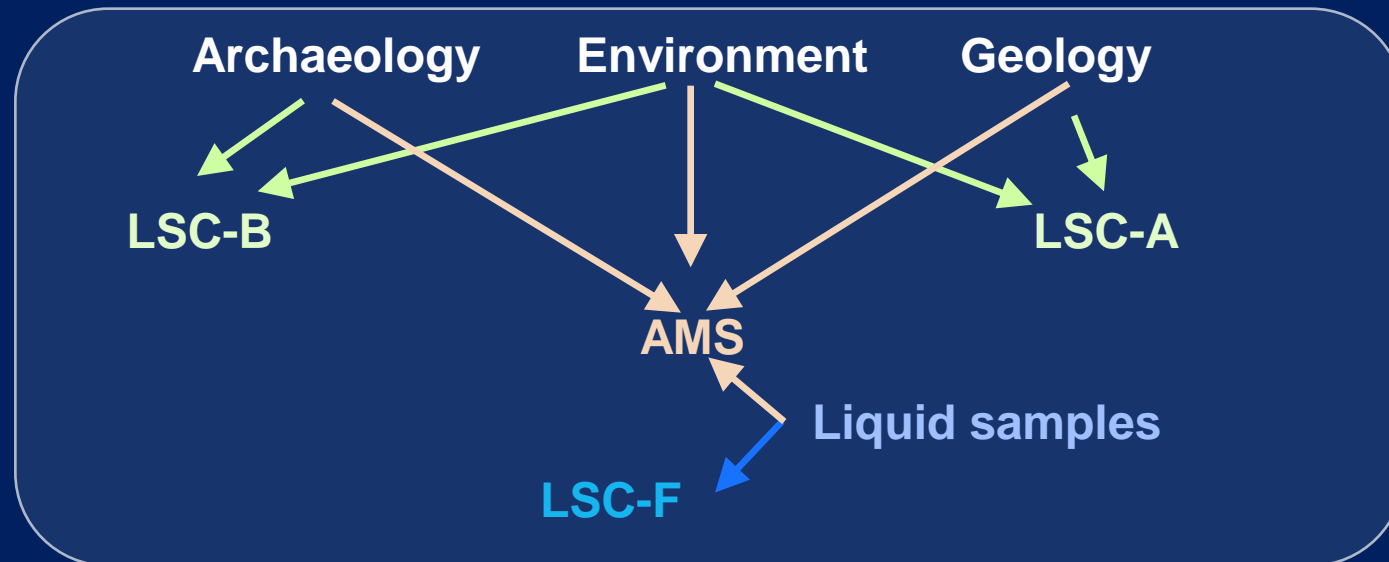
Assigning of unique laboratory preparation No to **unique sample No Z-xxxx**:
Byyy (Benzene synthesis), **Azzz** (AMS – graphitization),
Dqqq (CO₂ Direct Absorption), **Fccc** (liquid fuel, oils etc);

Preparation (technique) decision – discussed with the customer prior to the sample submission/preparation

Technique decision → Amount, **LSC-B and A (grams)** or **AMS (mg)**

Purpose of measuring (required precision)

Sample type



Price! → LSC-A, LSC-B, AMS → higher precision – higher price

MEASUREMENT METHODS

Radiometric – number of decays per time (i.e., decay rate) of ^{14}C per mass of carbon

required mass of C: 1 - 5 g

Required mass of samples: 10 - 50 g

Gas proportional counting (**GPC**)

Liquid scintillation counting (**LSC**);

LSC-A and LSC-B

Accelerator Mass Spectrometry (AMS) – number of ^{14}C atoms is counted, together with the number of ^{12}C and ^{13}C

Required mass: <2 mg C, <1 g sample

- low natural abundance of ^{14}C relative to ^{12}C (10^{-10} %)
 - low specific activity (226 Bq/kg of carbon in modern samples) low energy of electrons (<156 keV)
- very sensitive low-level radiometric measurement techniques have been developed, as well as the appropriate sample preparation procedures



LSC measurement: 1-4 g of carbon:

Wood, leaves, textile: 20-50 g

Charcoal: 10-15 g

Bone: 300-500 g

Soil: 30-500 g

Water (bicarbonate): 50-100 L

All types of samples

Mechanical pretreatment – inspection and
mechanical cleaning, mulching, milling

Solvent extraction

Chemical pretreatment:

Organic samples: wood, charcoal, textile (ABA):

Removing of carbonates,
Fulvic acids
4% HCl, 5 h, 80-90°C

Removing of humic acids,
mold, 2 % NaOH, 1-4 h, 80-
90°C

Removing of CO₂,
4% HCl, 1 h, 80-90°C

Neutralisation

Drying

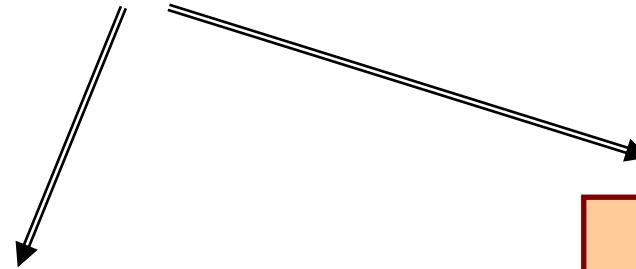
Solvent extraction (wood, soil organics,
peat and charcoal, from specific
environments)

Neutralization

Pretreatment
A — B — A

Carbonization

Combustion



Removing of resins and waxes ^{1,2}

soxhlet extractor



contaminant is suspected
its identity unknown

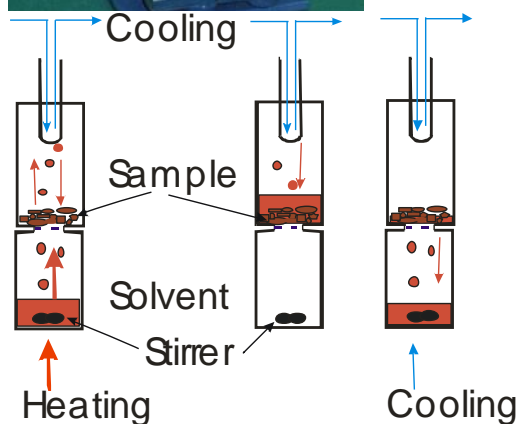
acetone (40–50 °C)

methanol (40–50 °C)

chloroform (room temp.)

water wash (40–50 °C)

Drying
ABA



Solvent	Boiling Temp. °C	Temp. set. (°C)	dissolves:
Tetrahydro furane (THF)	65	140	Cellulose acetate, (poly)vinyl acetate, epoxy resin (e.g. Araldit)
Chloroform	61	140	Beeswax, polyethylene glycol, ketone resin, THF
Petrolether	40-60	100	Fat, Chloroform
Acetone	56	120	Cellulose acetate, petrolether
Methanol	65	165	Shellack, acetone
Water	100		Methanol

3 cycles, 75 ml, 5 min filtration time;
each extraction takes ~60 min

¹Bruhn, F., A. Duhr, et al. (2001). [Radiocarbon](#) **43**:229-237.

²Brock, F., Higham, T., et al. (2010). [Radiocarbon](#) **52**:103-112

Bones, extraction of collagen, Longin method

Longine (1971) Nature 230:241-242

Bone amount (g)	Volume of added HCl (mL) Processing time: 5 min each step			Total volume (mL)
80	125	275	400	800
100	150	350	500	1000
200	300	700	1000	2000
250	400	850	1250	2500
300	450	1050	1500	3000
325	500	1150	1500	3250
350	550	1220	1750	3500
400	600	1400	2000	4000

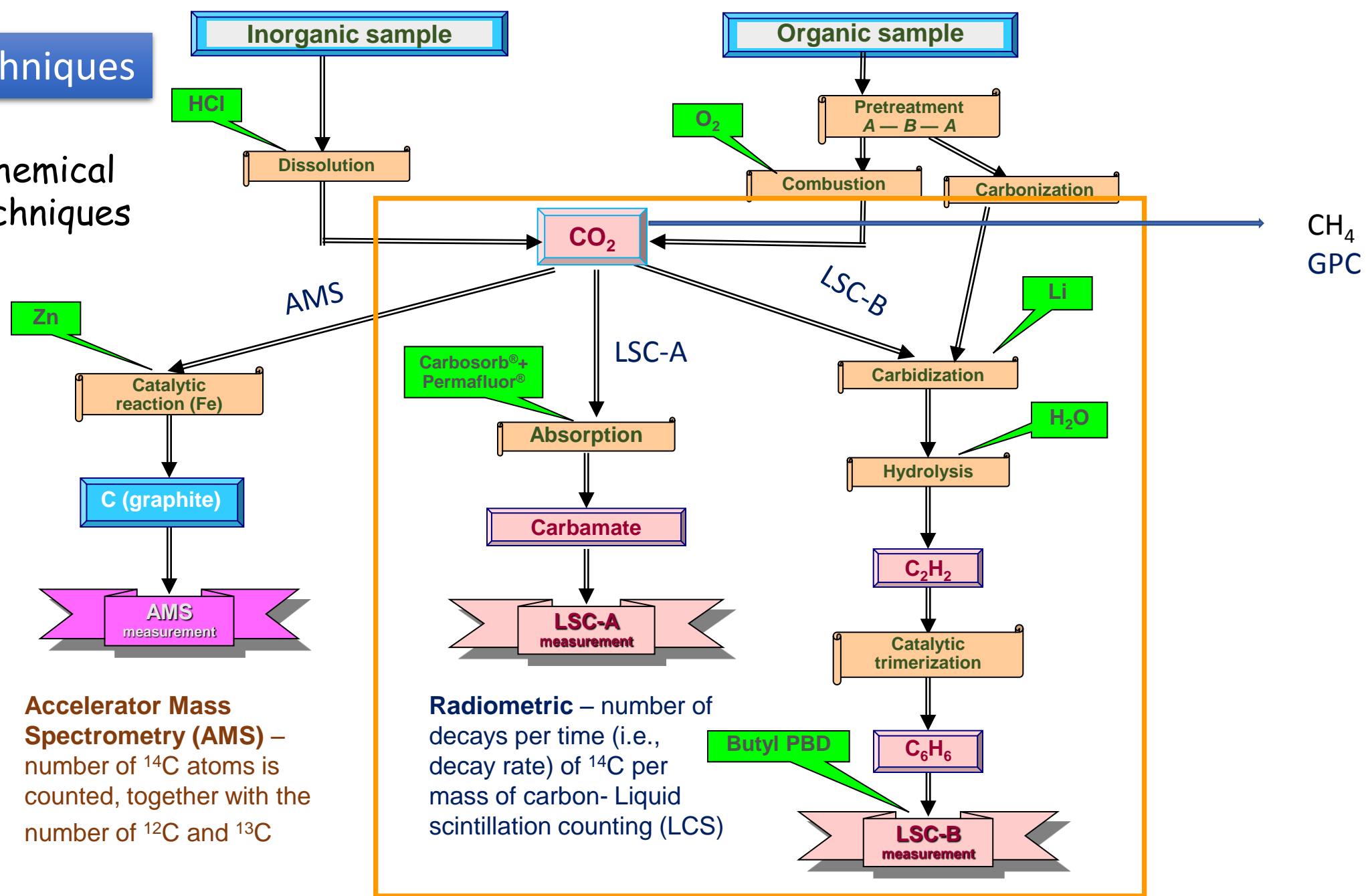
Decanting → Heating of residue (app. 1L, ~90°C, pH = 3, 18 h),
steering, reflux

Filtration → drying of bone collagen(UV) → **Combustion**

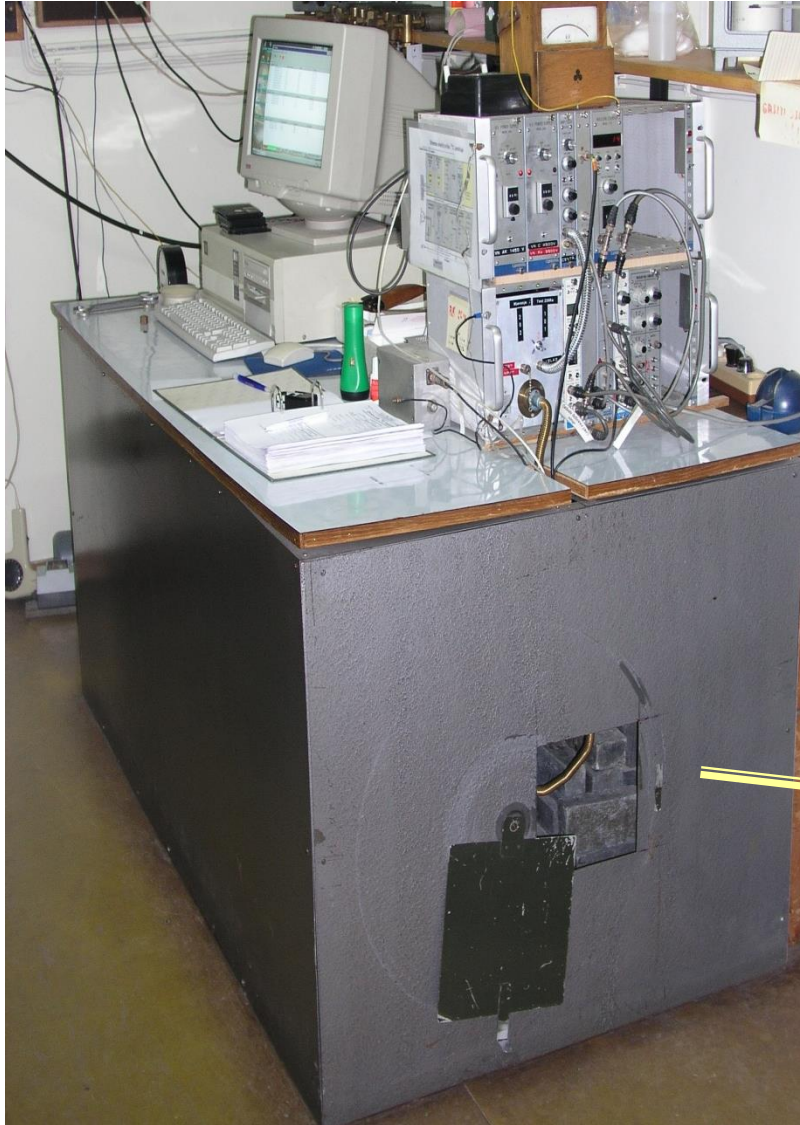
Currently – no LSC for bone samples, only AMS!

¹⁴C dating techniques

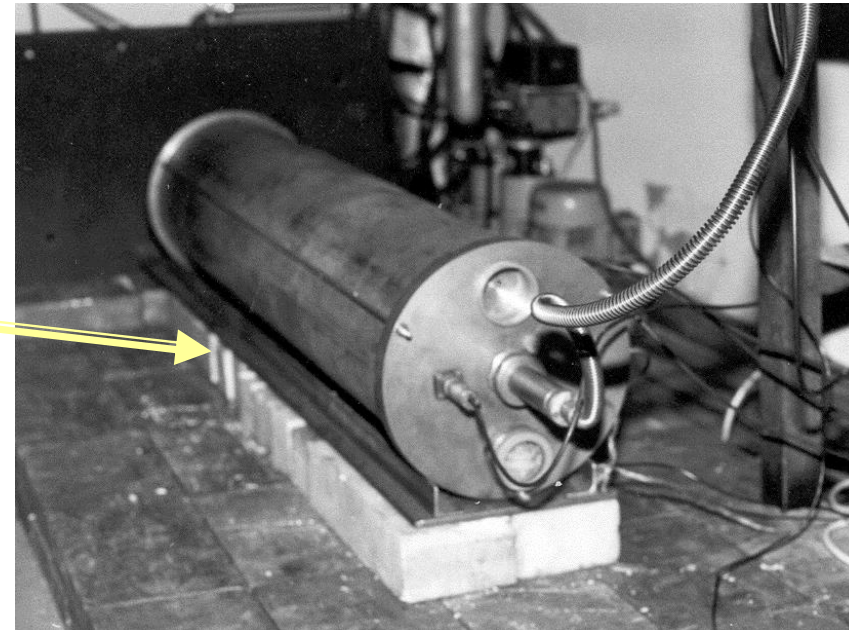
Flowchart of chemical preparation techniques



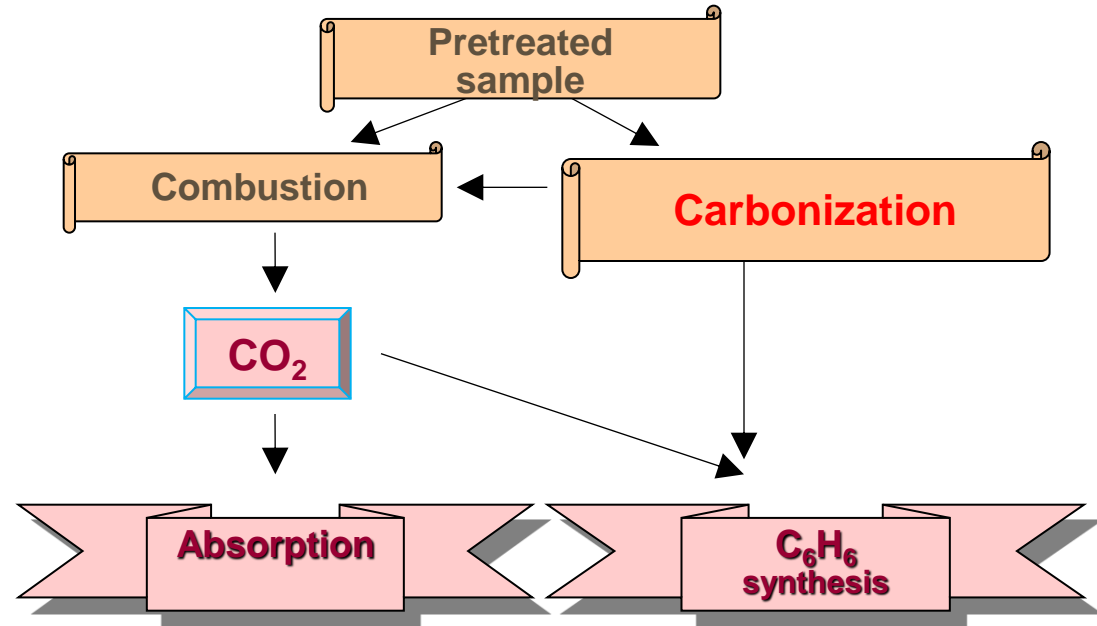
GPC – Gas proportional counting



- Counting gas (CH_4) → sample and detection medium
- β particles from decay ionize gas → primary electrons
- electron avalanches are produced in strong electric field → signal



Organic samples



**Carbonisation: wood, plants, biological samples
(i.e. corn, apples)**

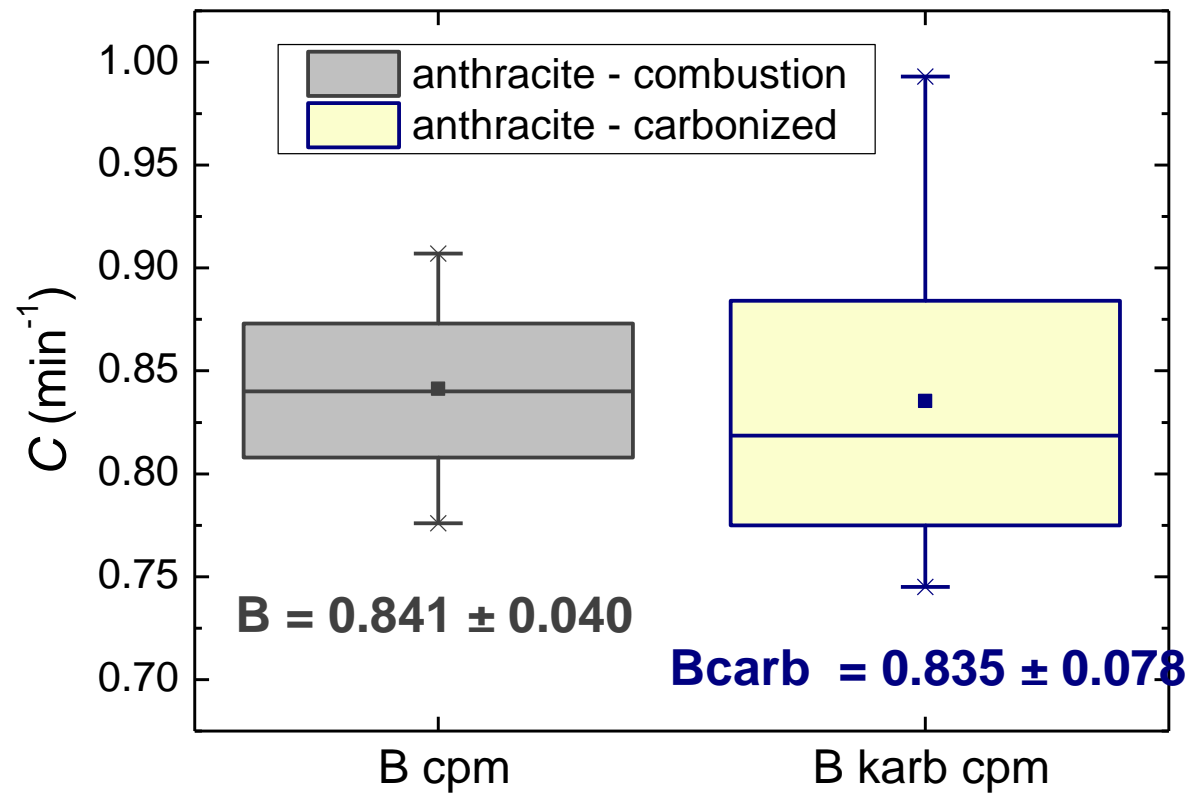
600°C, 15 min

Relatively big samples, mass reducing 50-70%

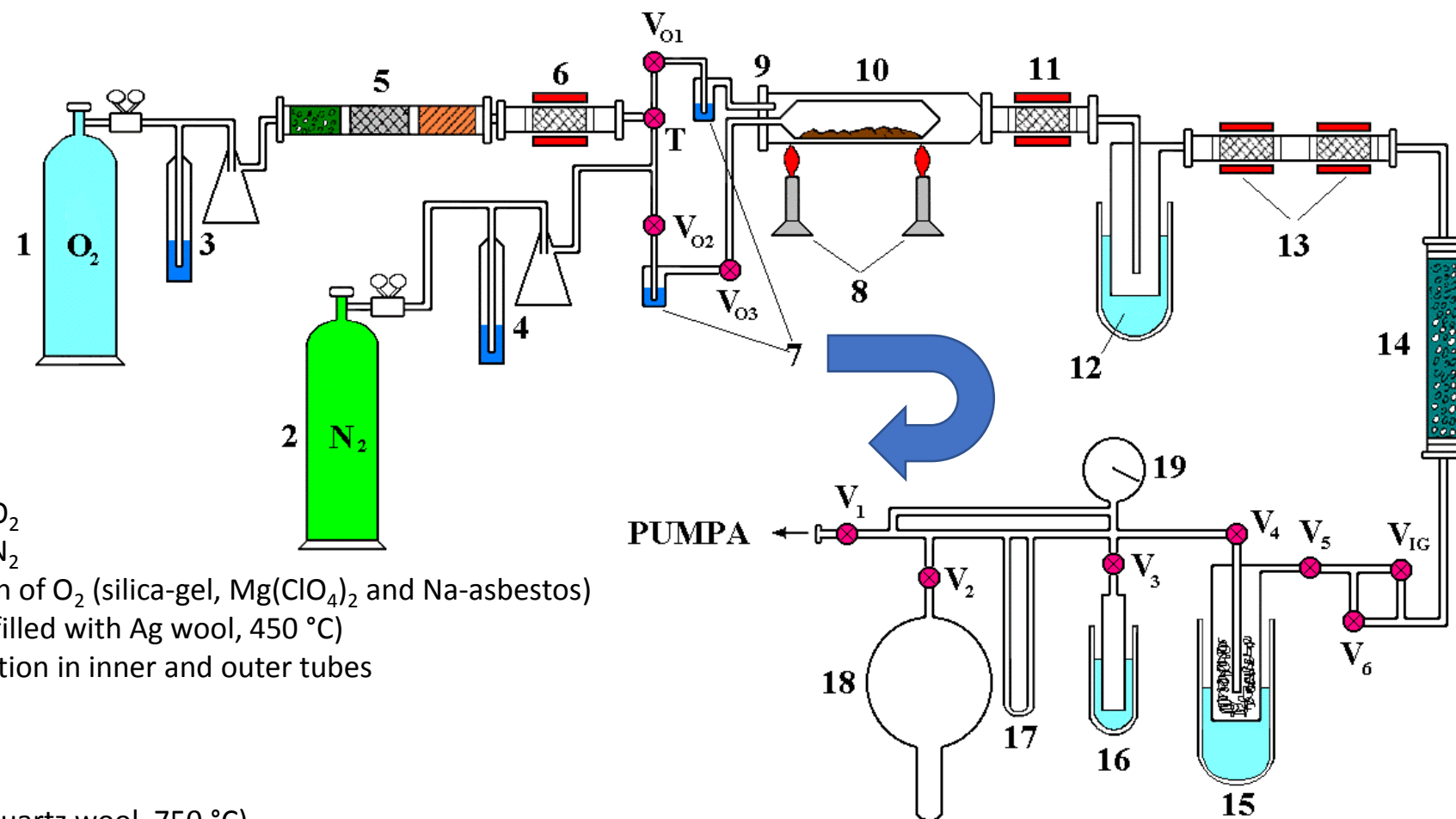
Removing of water (alternative to pyrolysis)

**More economic combustion and benzene
synthesis**

Comparison of count rates of combusted and carbonized ^{14}C -free sample

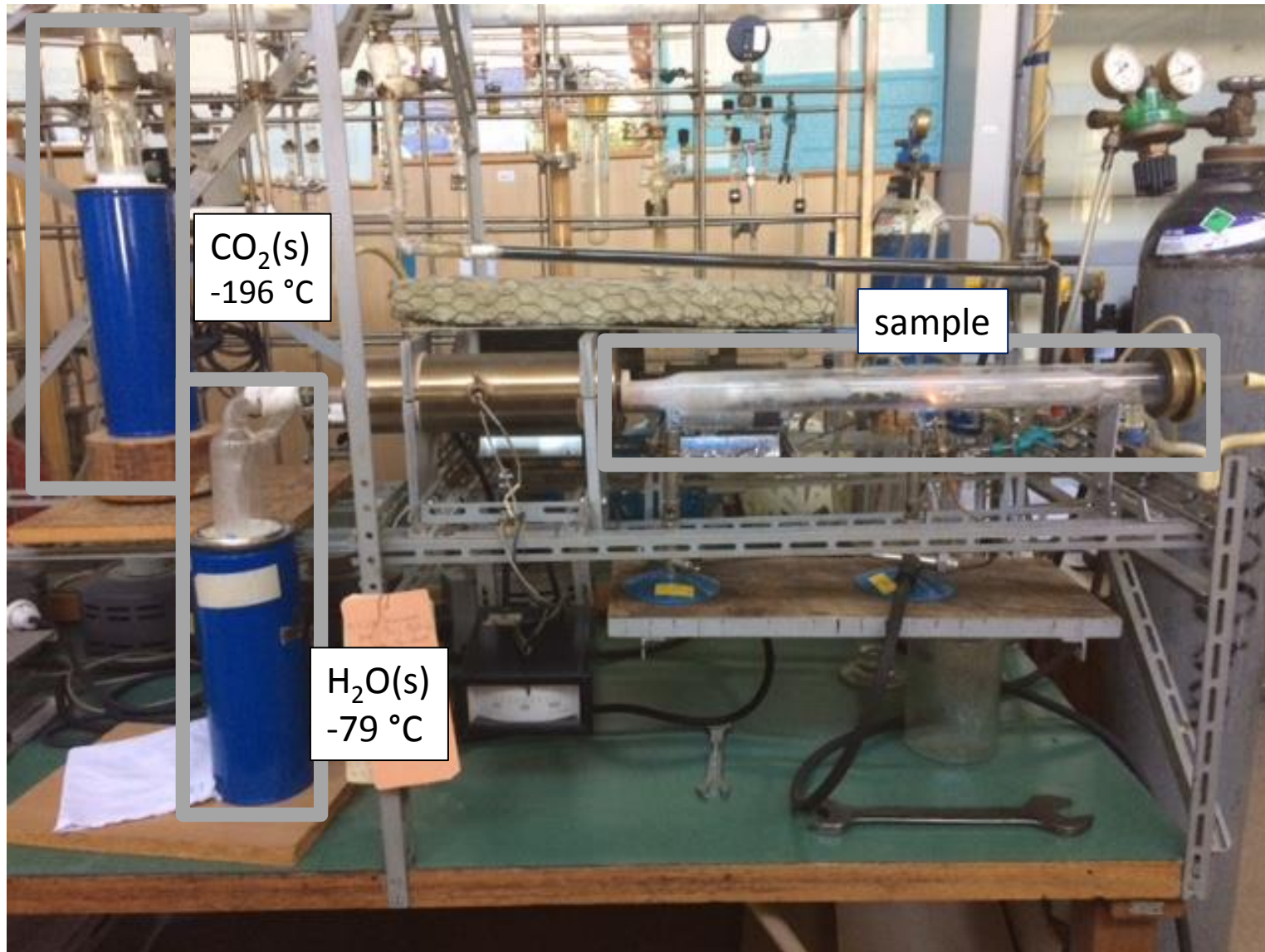


Combustion line for organic samples

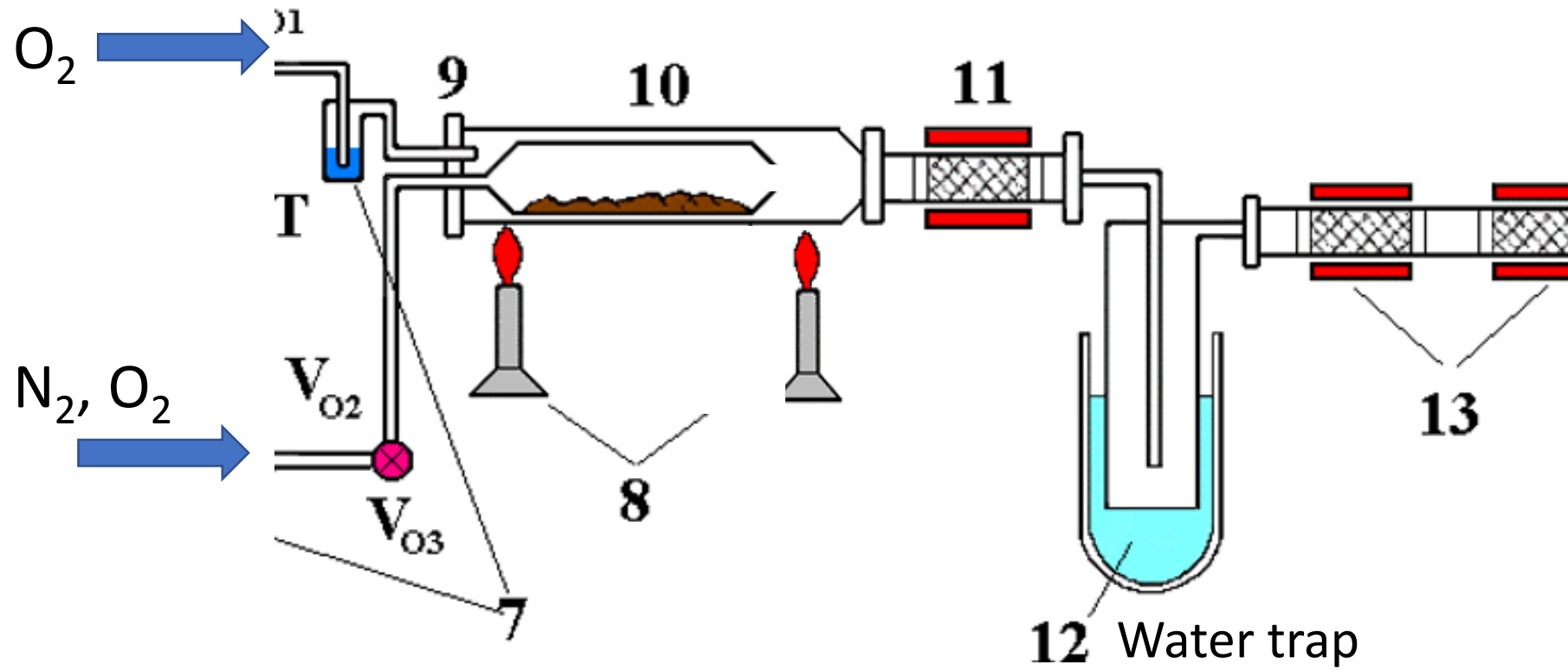


- 1 pressured tank with O₂
- 2 pressured tank with N₂
- 3 flow-rate indicator – bubbler, O₂
- 4 flow-rate indicator – bubbler, N₂
- 5 absorption tube for purification of O₂ (silica-gel, Mg(ClO₄)₂ and Na-asbestos)
- 6 furnace for purification of O₂ (filled with Ag wool, 450 °C)
- 7 bubblers for O₂/ N₂ flow indication in inner and outer tubes
- 8 burners
- 9 metal cap
- 10 quartz tube with the sample
- 11 oxidation furnace (filled with quartz wool, 750 °C)
- 12 water trap (-80 °C)**
- 13 furnace for purification of CO₂ (filled with Ag wool, 450 °C)
- 14 absorption tube for purification of CO₂ (filled with MnO₂)
- 15 trap for CO₂ (filled with, Cu cuttings, -196 °C)**
- 16 metal reservoir for CO₂ collection and storage
- 17 Hg-manometer for measurement of CO₂ pressure
- 18 glass bulb for CO₂ collection, volume of 12 L
- 19 digital pressure-meter

Combustion line



Combustion line - detail



Various commercially available furnaces



(a)



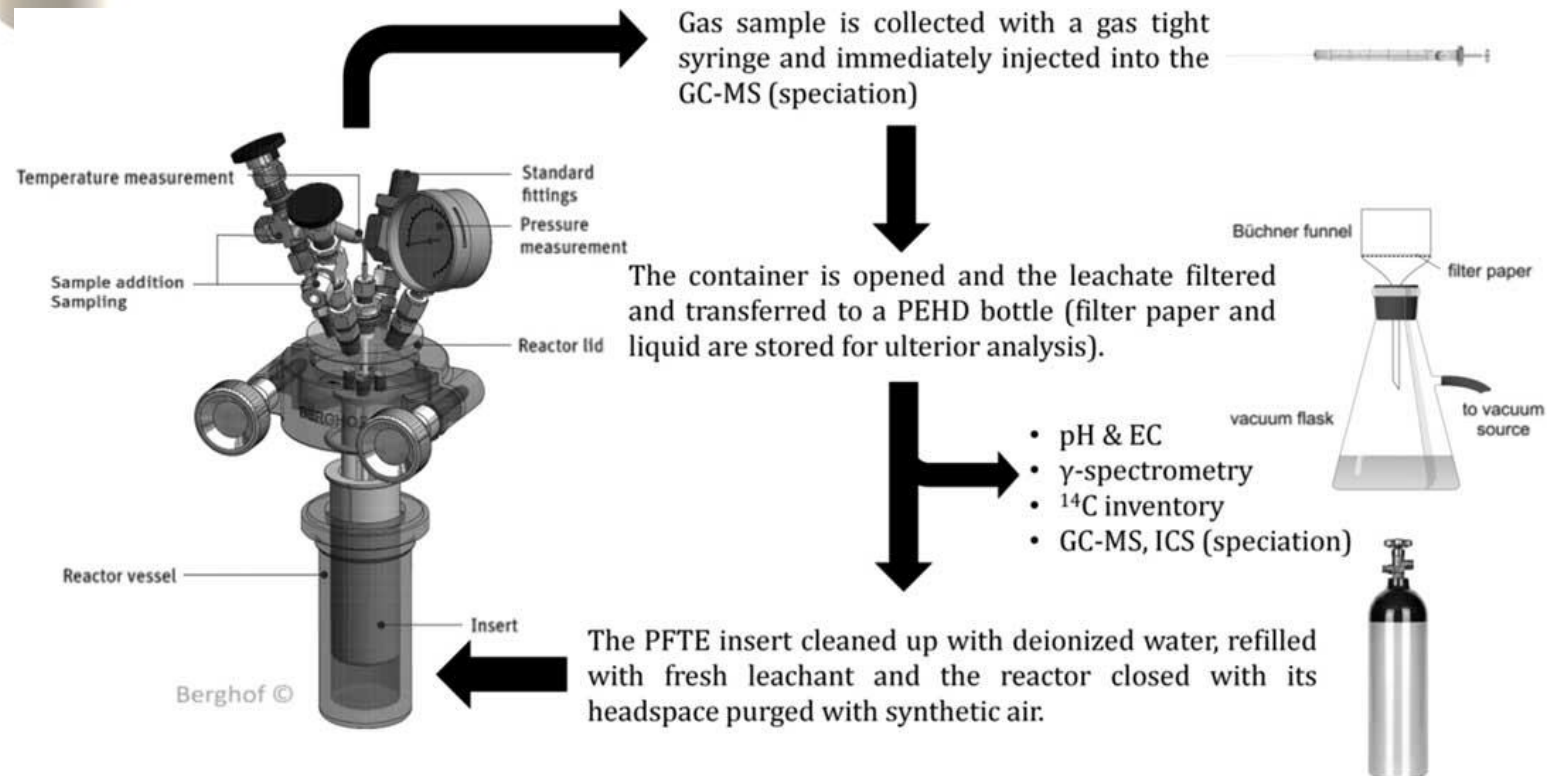
(b)



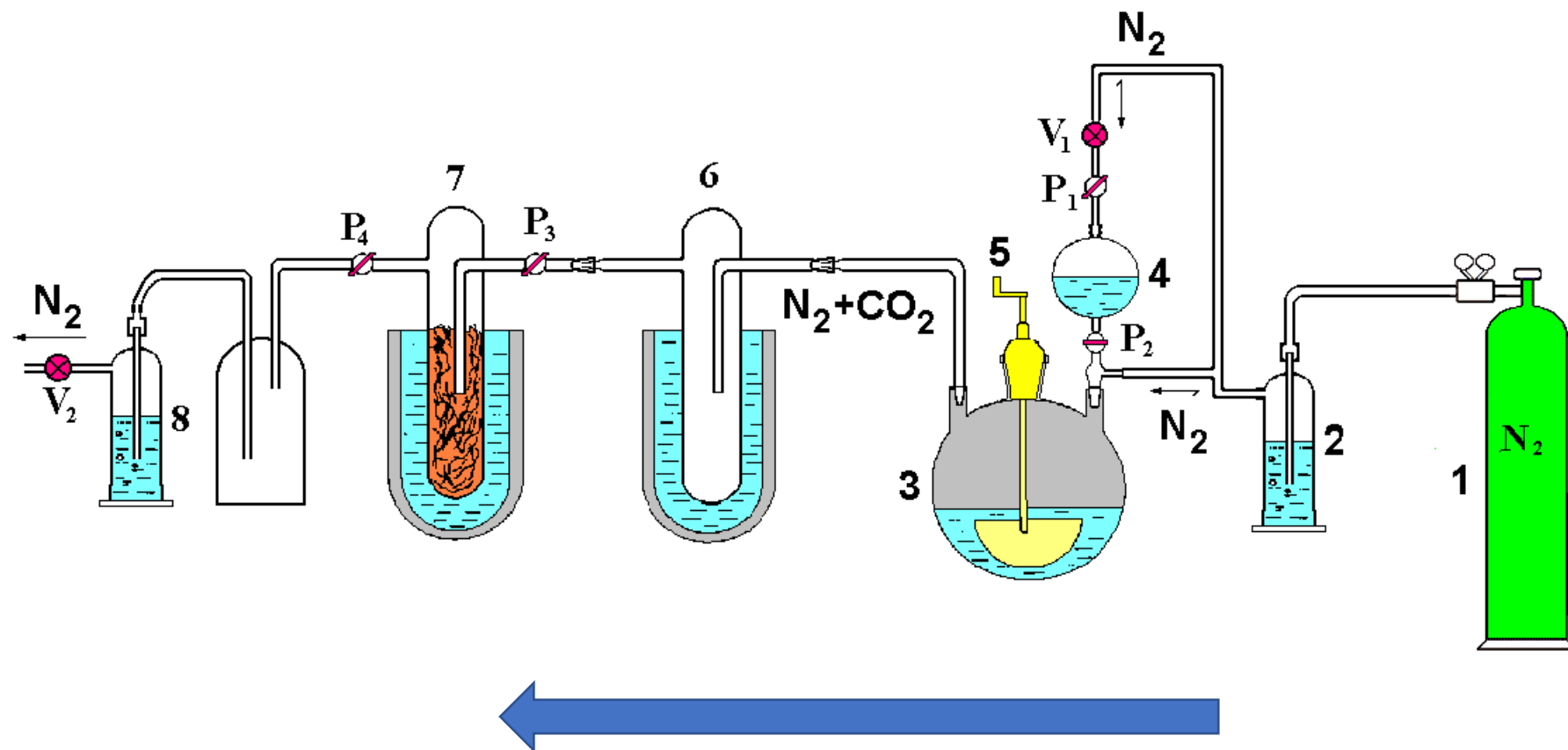
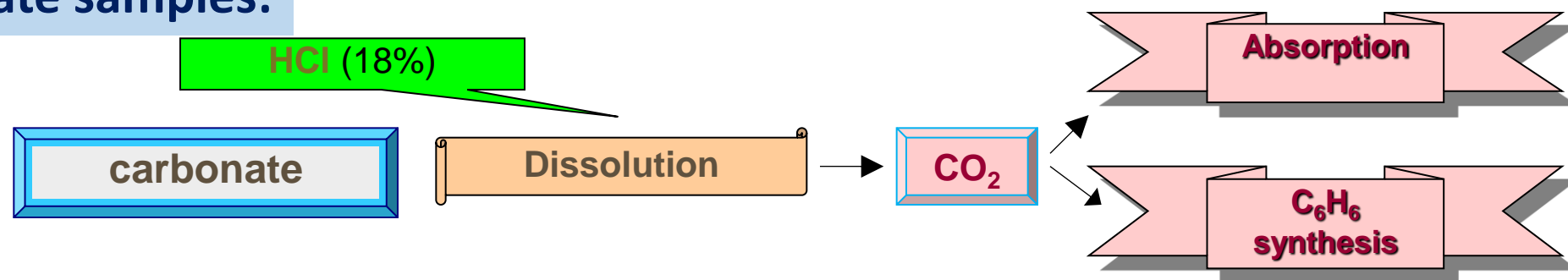
Various commercially available „bomb” reactors



High-pressure reactor „bomb”



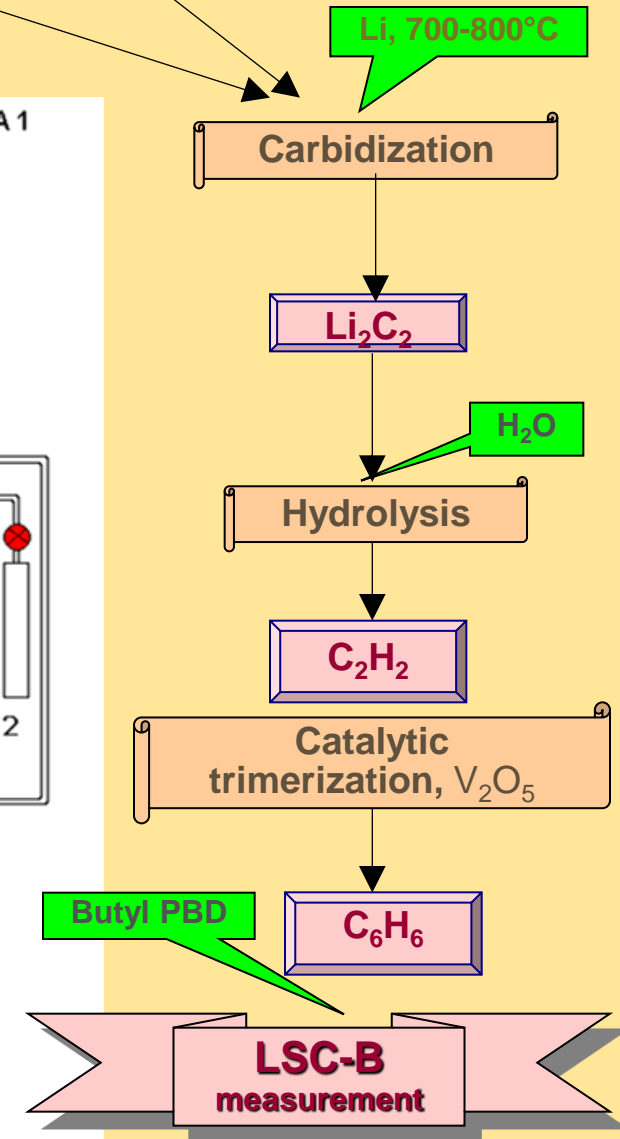
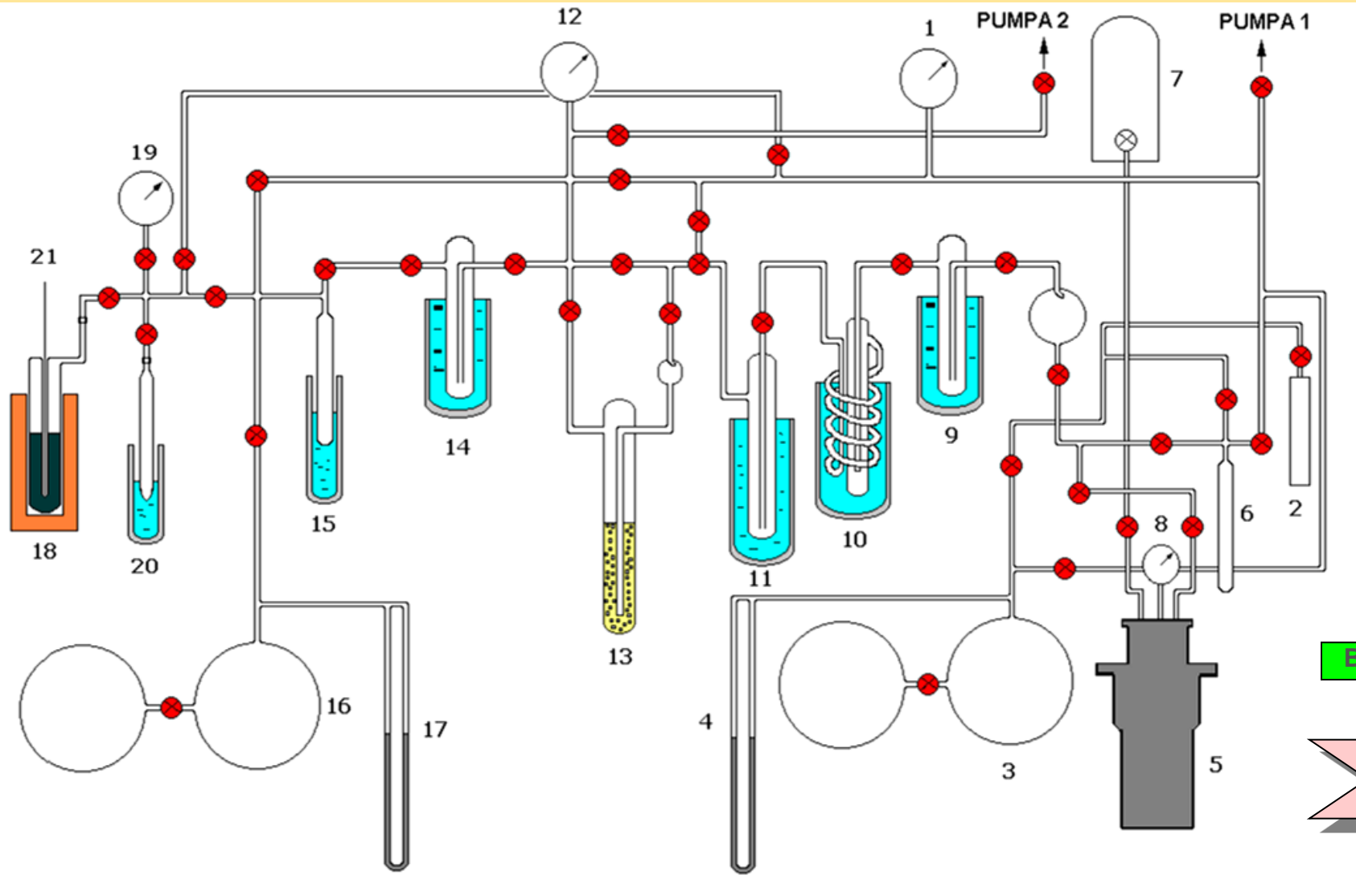
Carbonate samples:



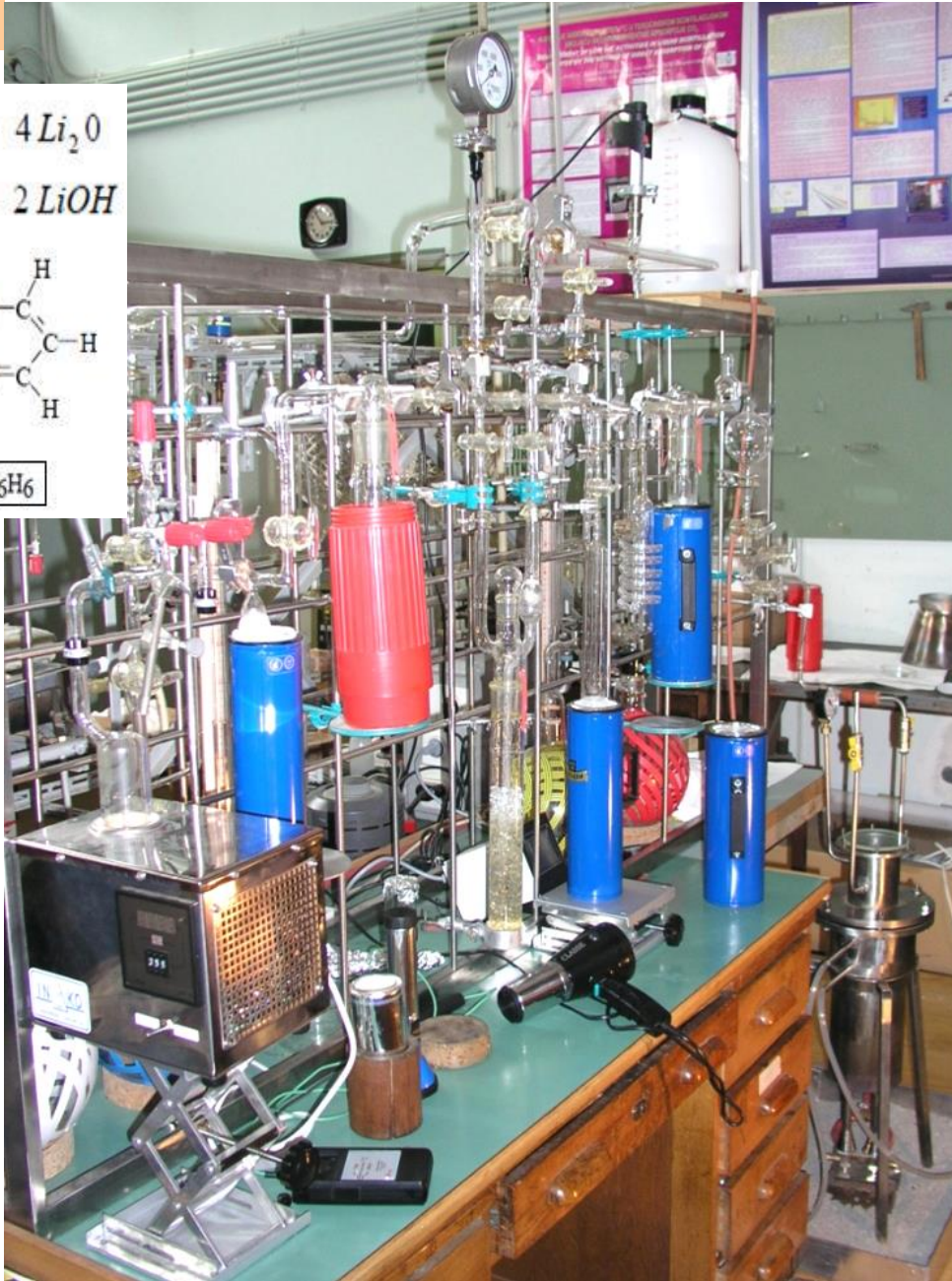
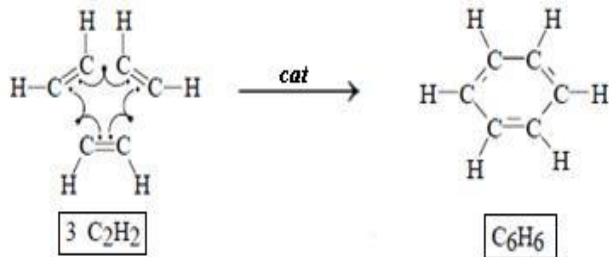
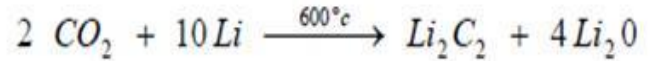
Line at RBI



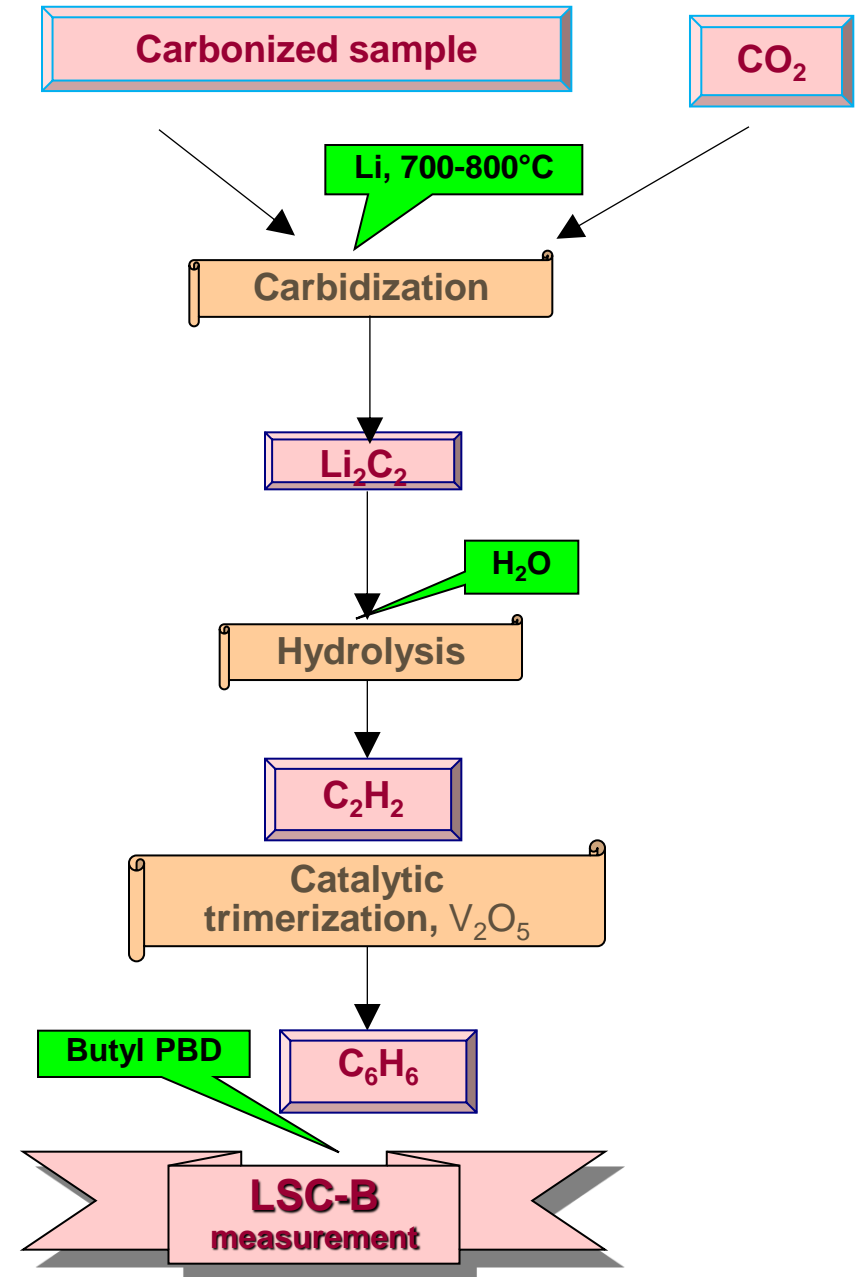
LSC-B – Benzene synthesis

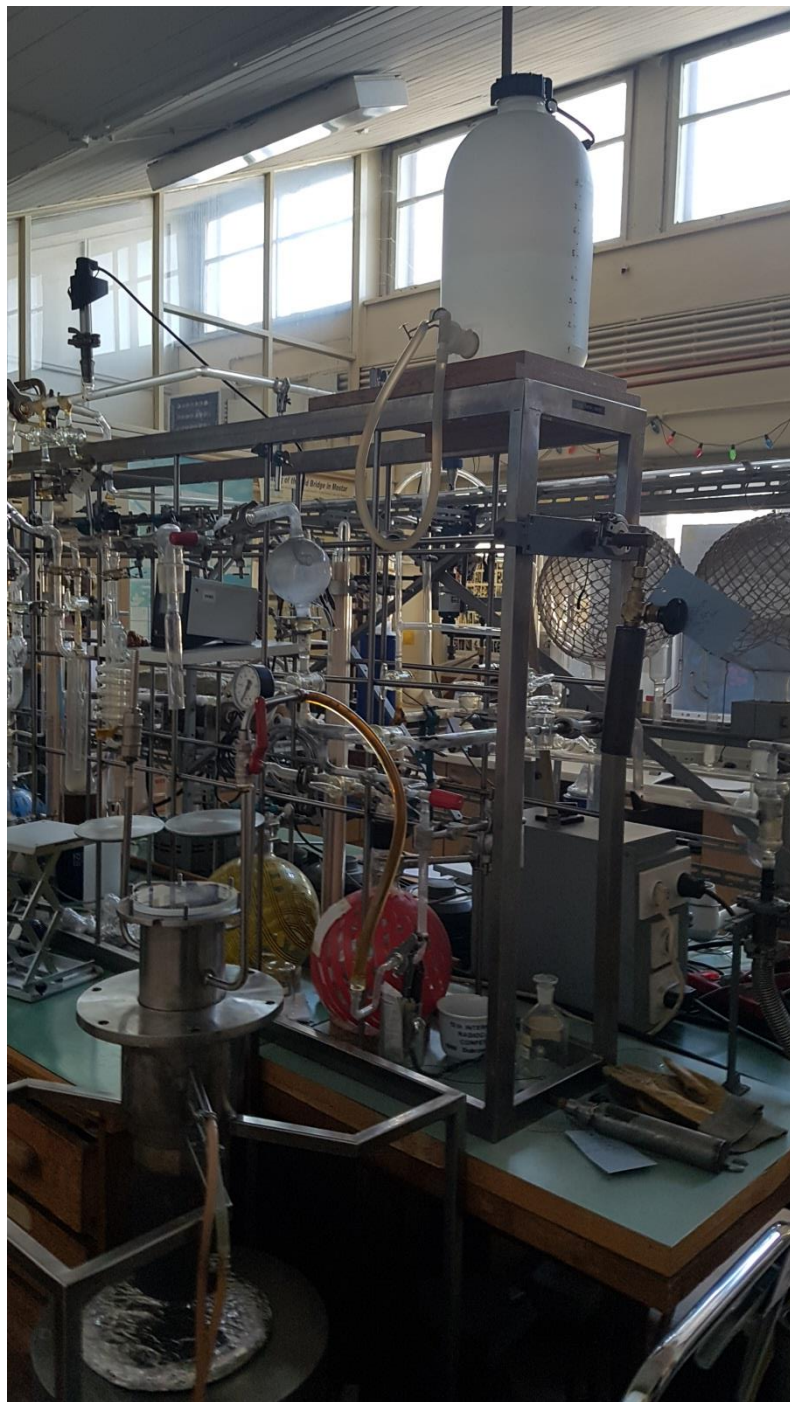


LSC-B



Line at RBI

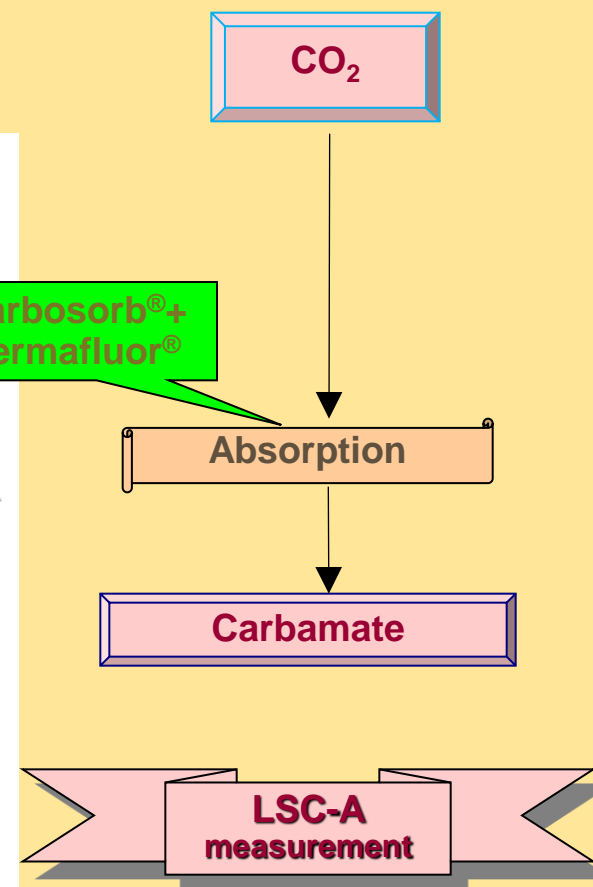
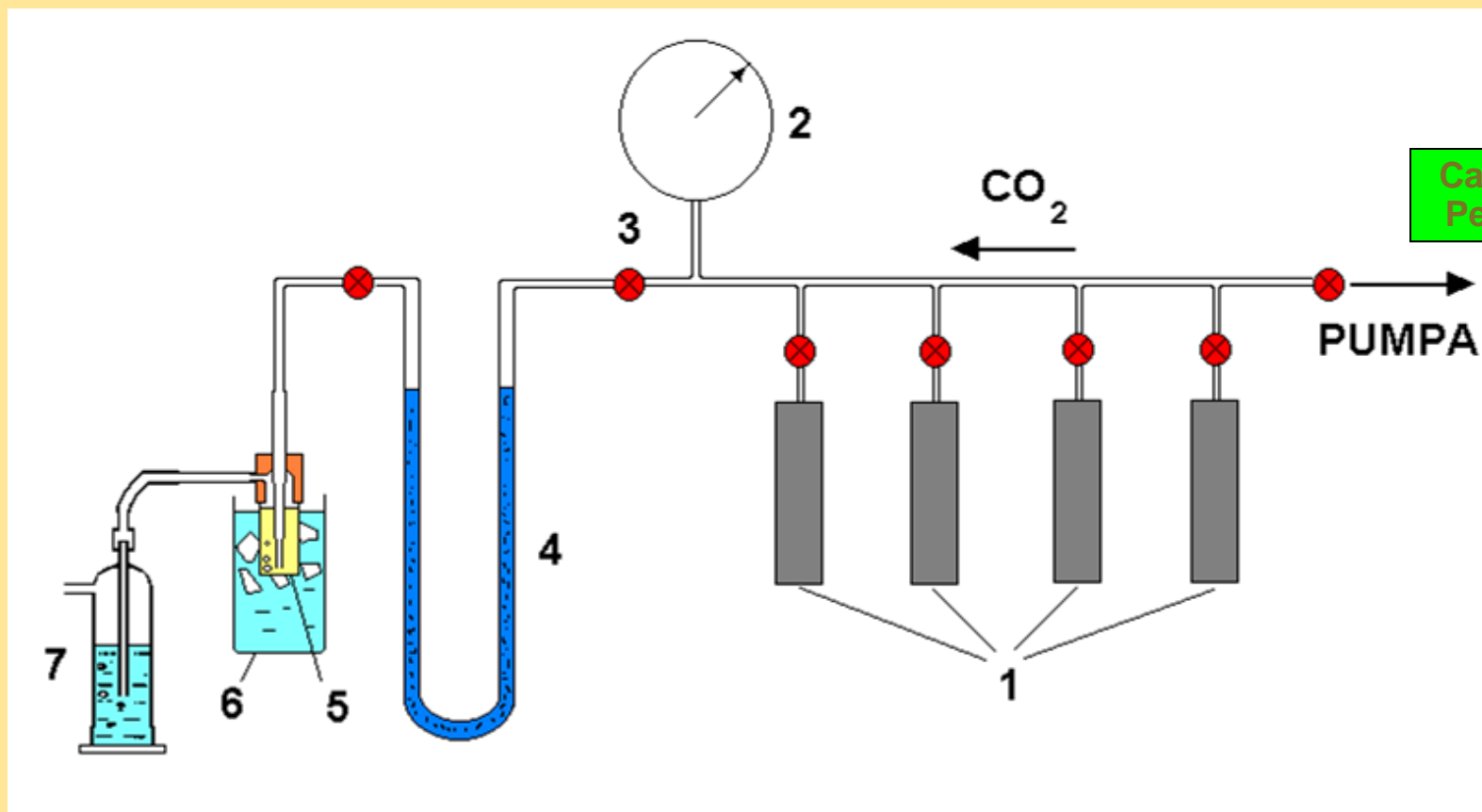




Line at RBI



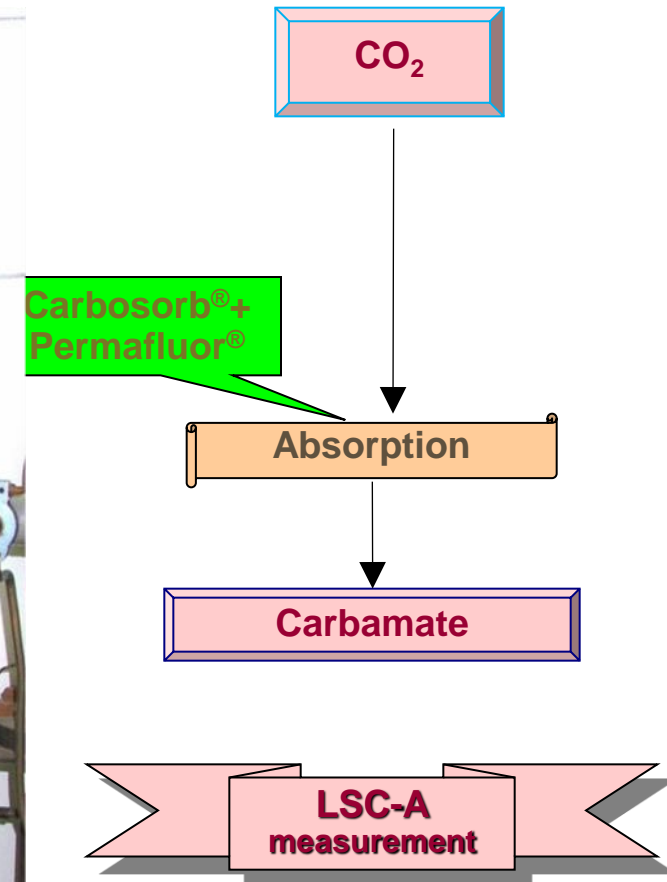
LSC-A – Absorption of CO₂



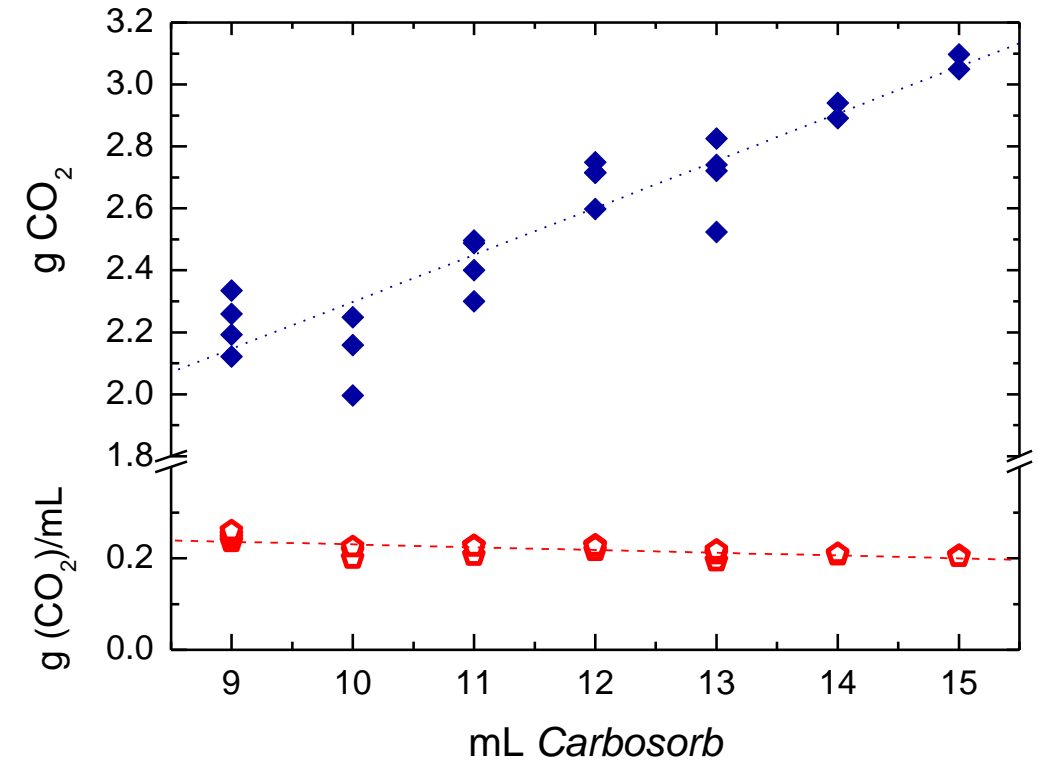
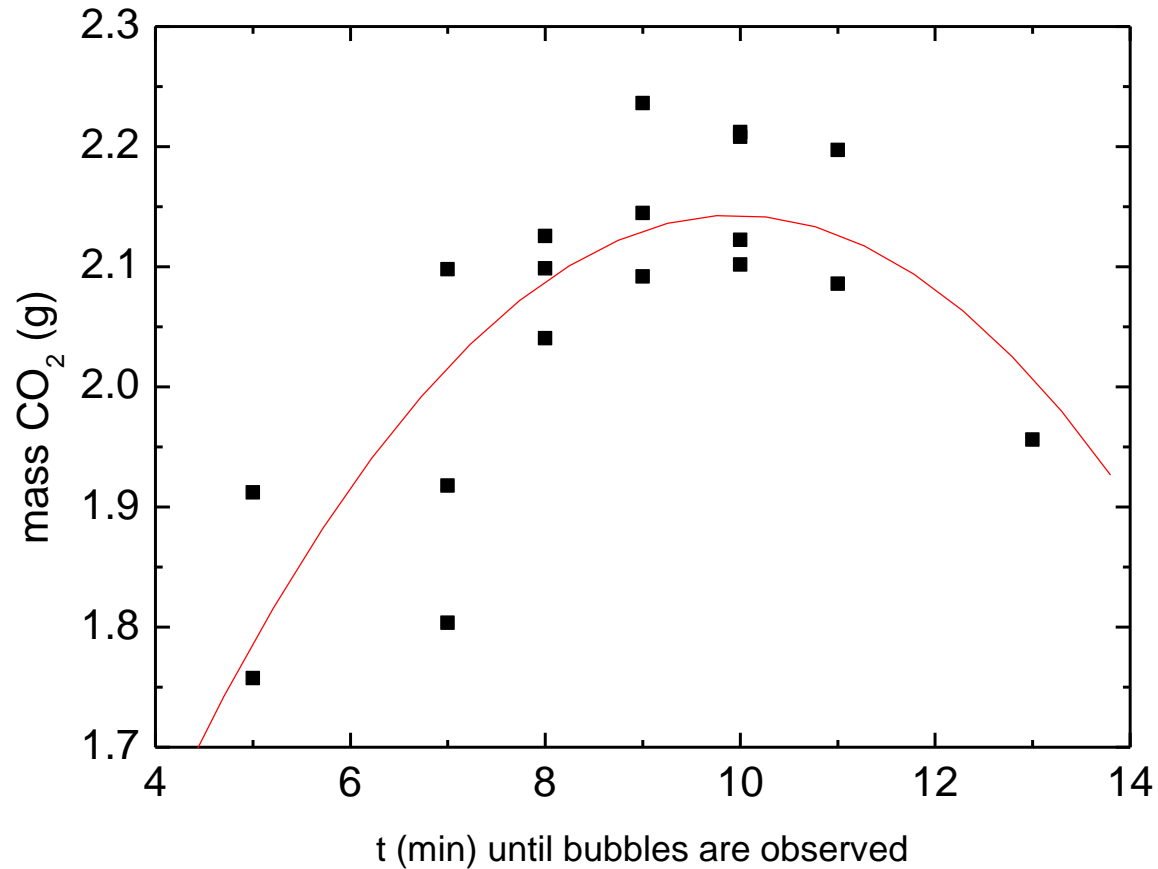
LSC-A



Line at RBI

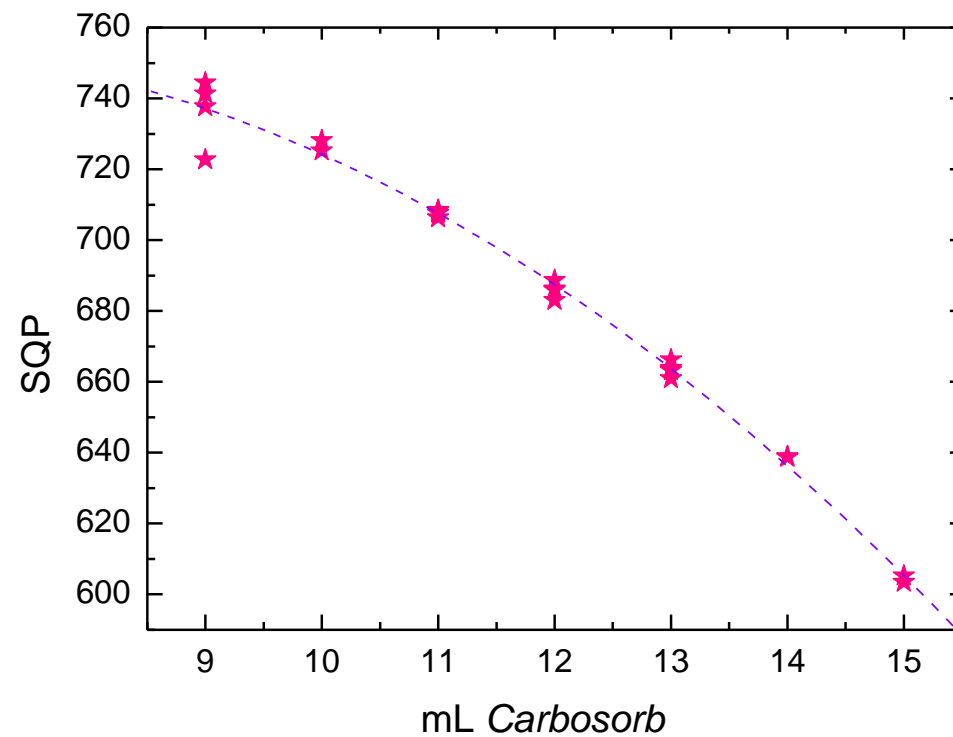
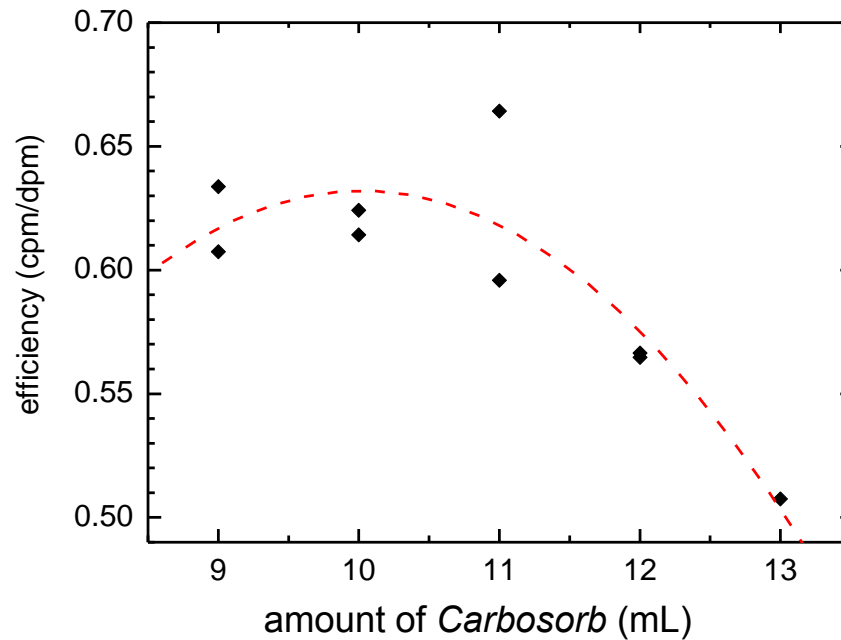
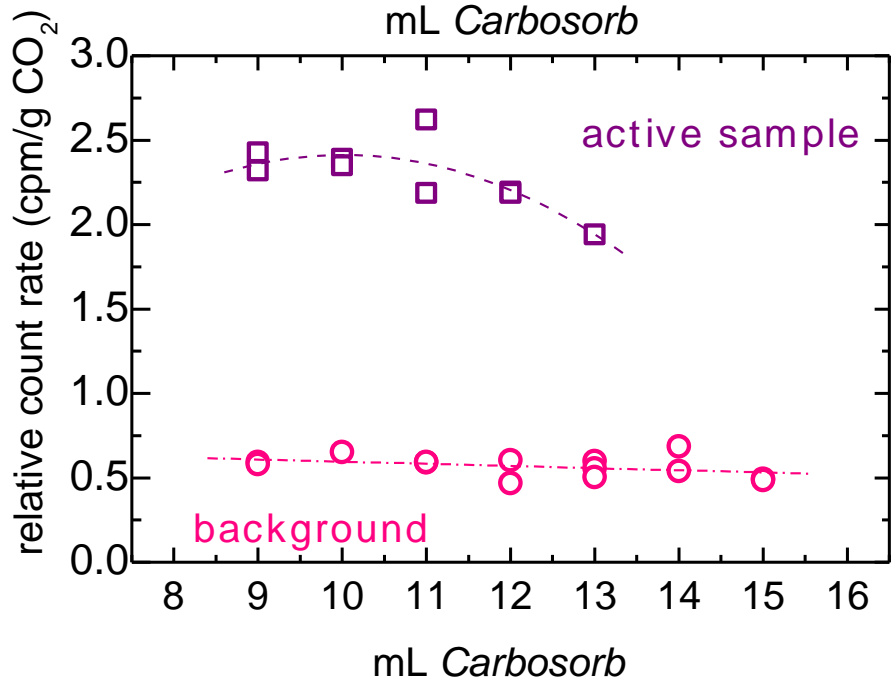
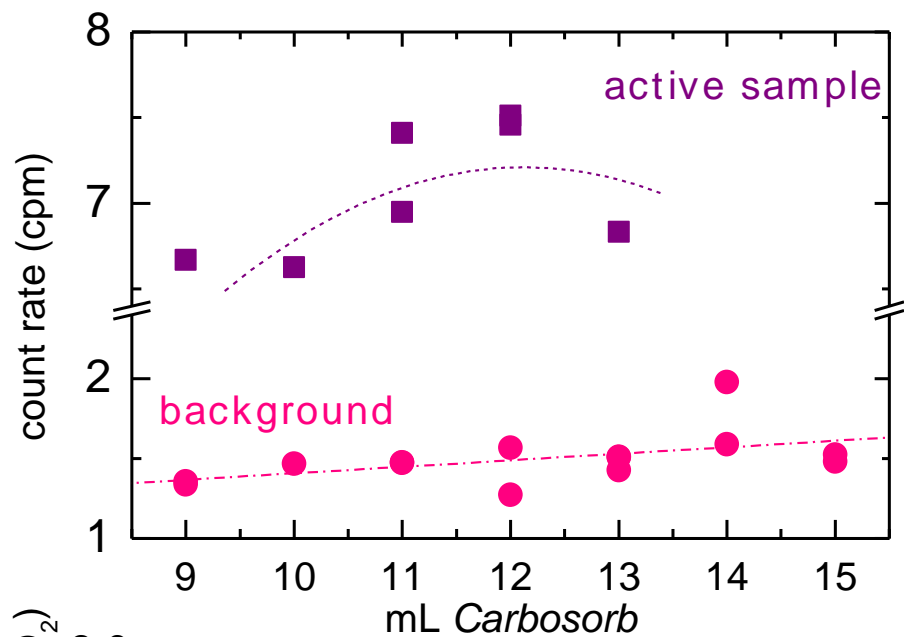


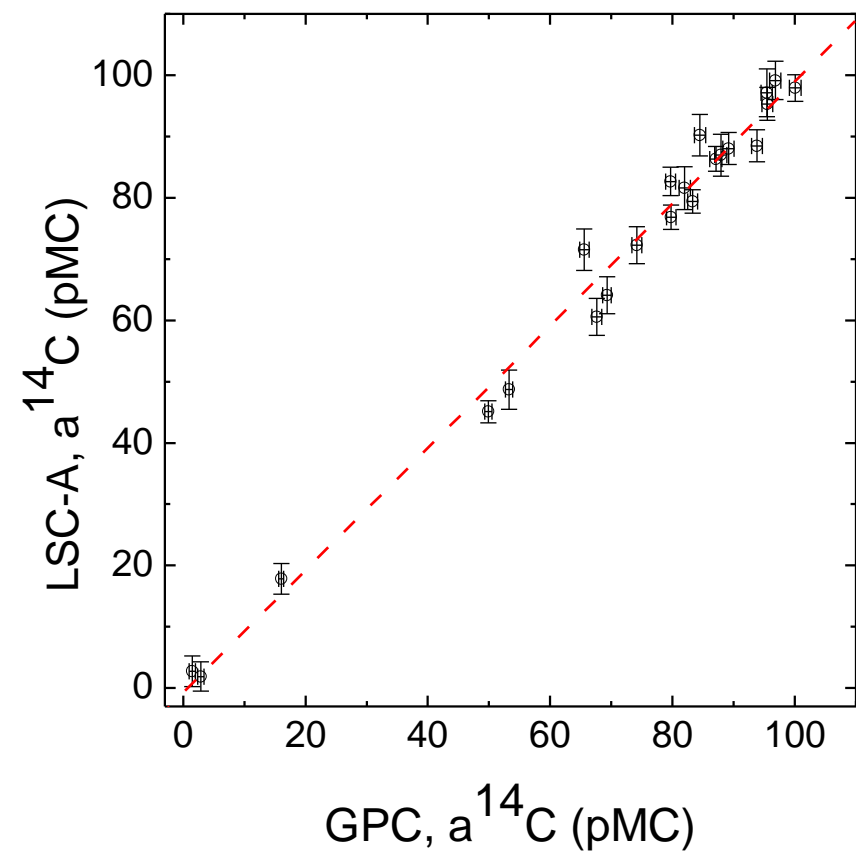
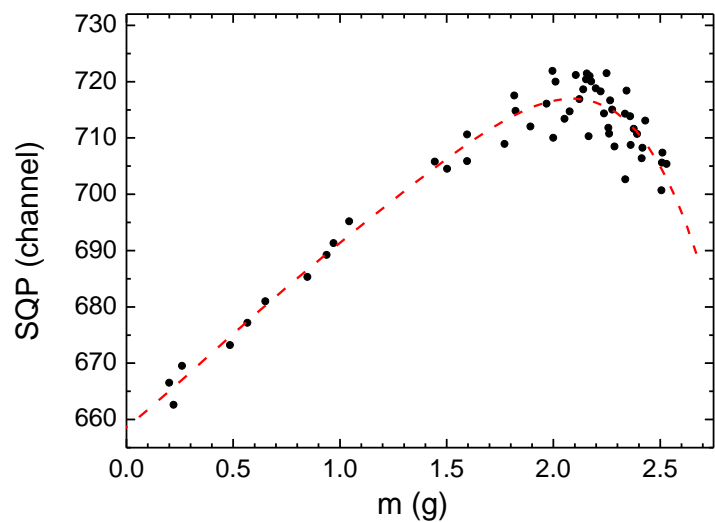
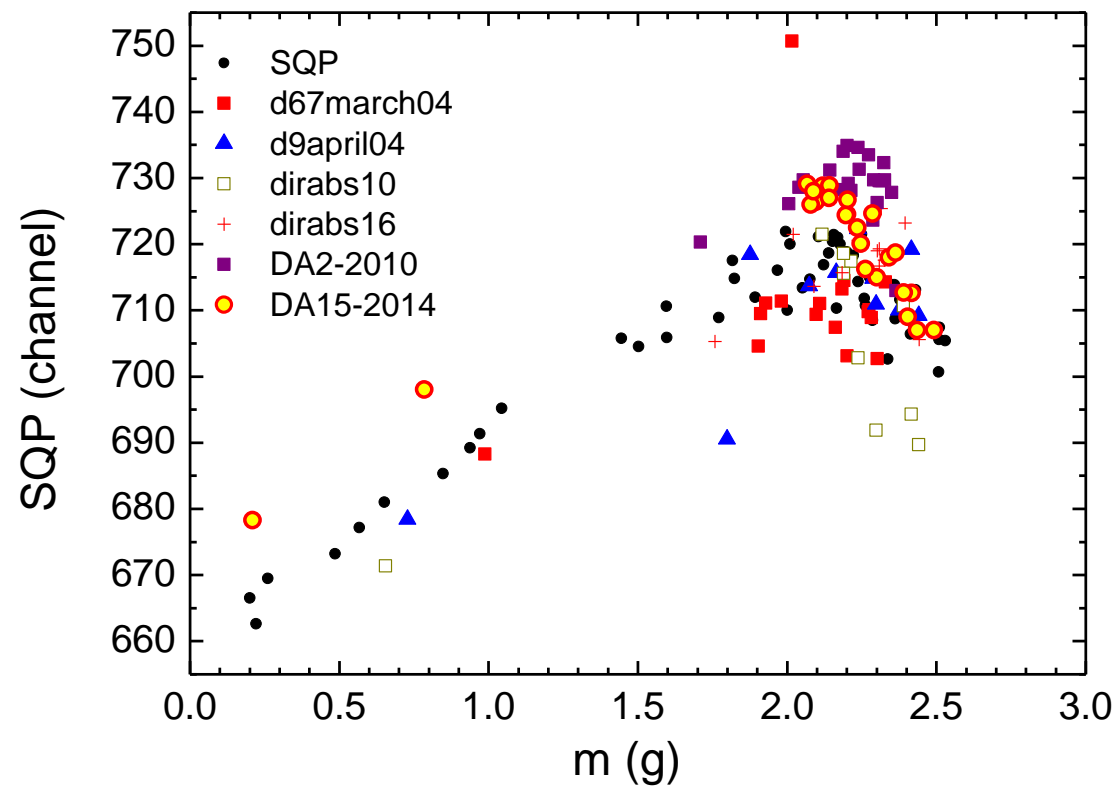
Validation of the method LSC-A



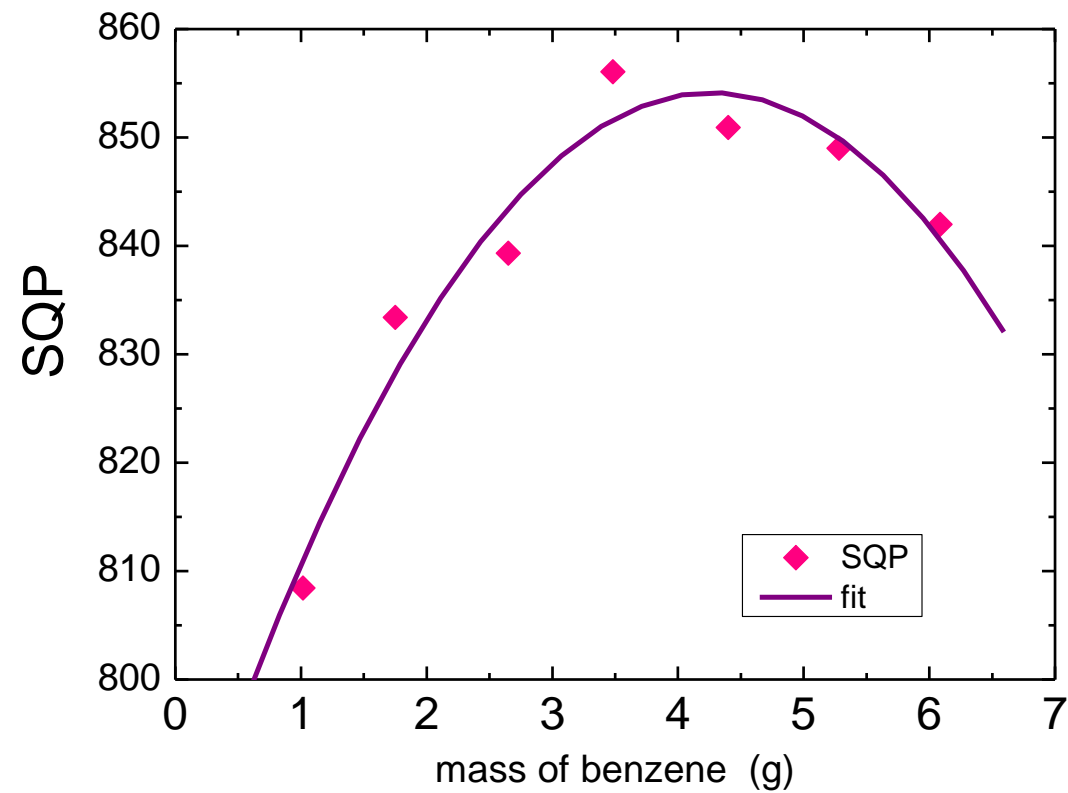
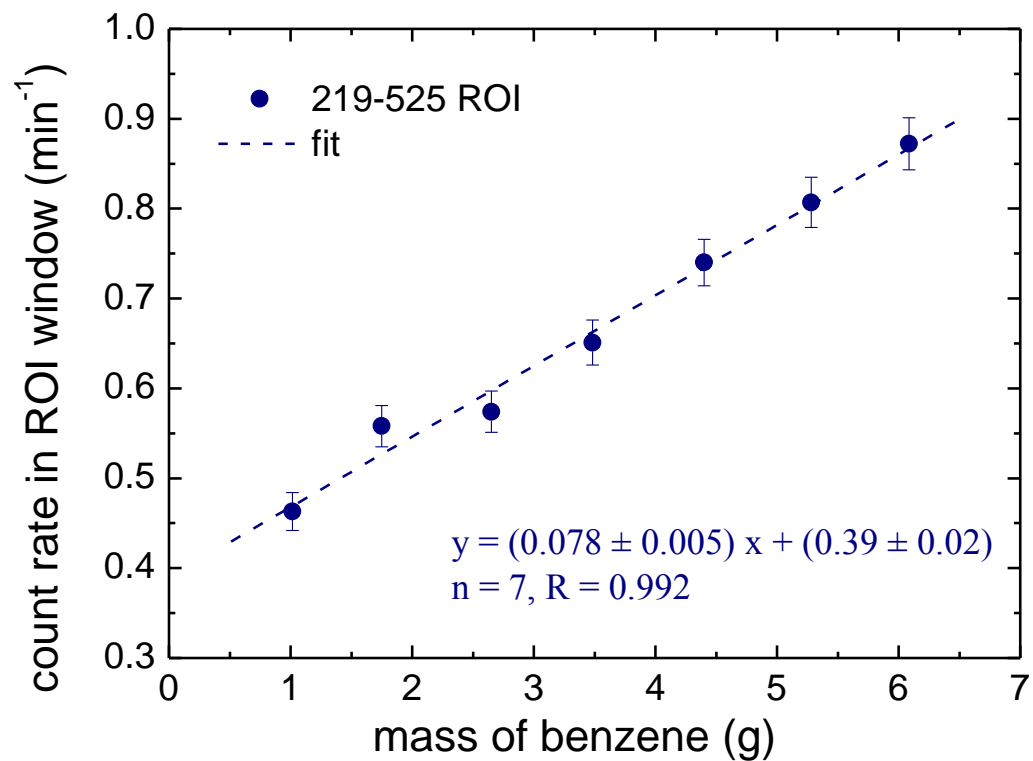
Horvatinčić, N; Barešić, J; Krajcar Bronić, I; Obelić, B. Measurement of Low ¹⁴C Activities in Liquid Scintillation Counter in the Zagreb Radiocarbon Laboratory. [Radiocarbon 46 \(2004\) 105-116](#)

Krajcar Bronić, I; Horvatinčić, N; Barešić, J; Obelić, B. Measurement of ¹⁴C activity by liquid scintillation counting. [Applied Radiation and Isotopes 67 \(2009\) 800-804](#)

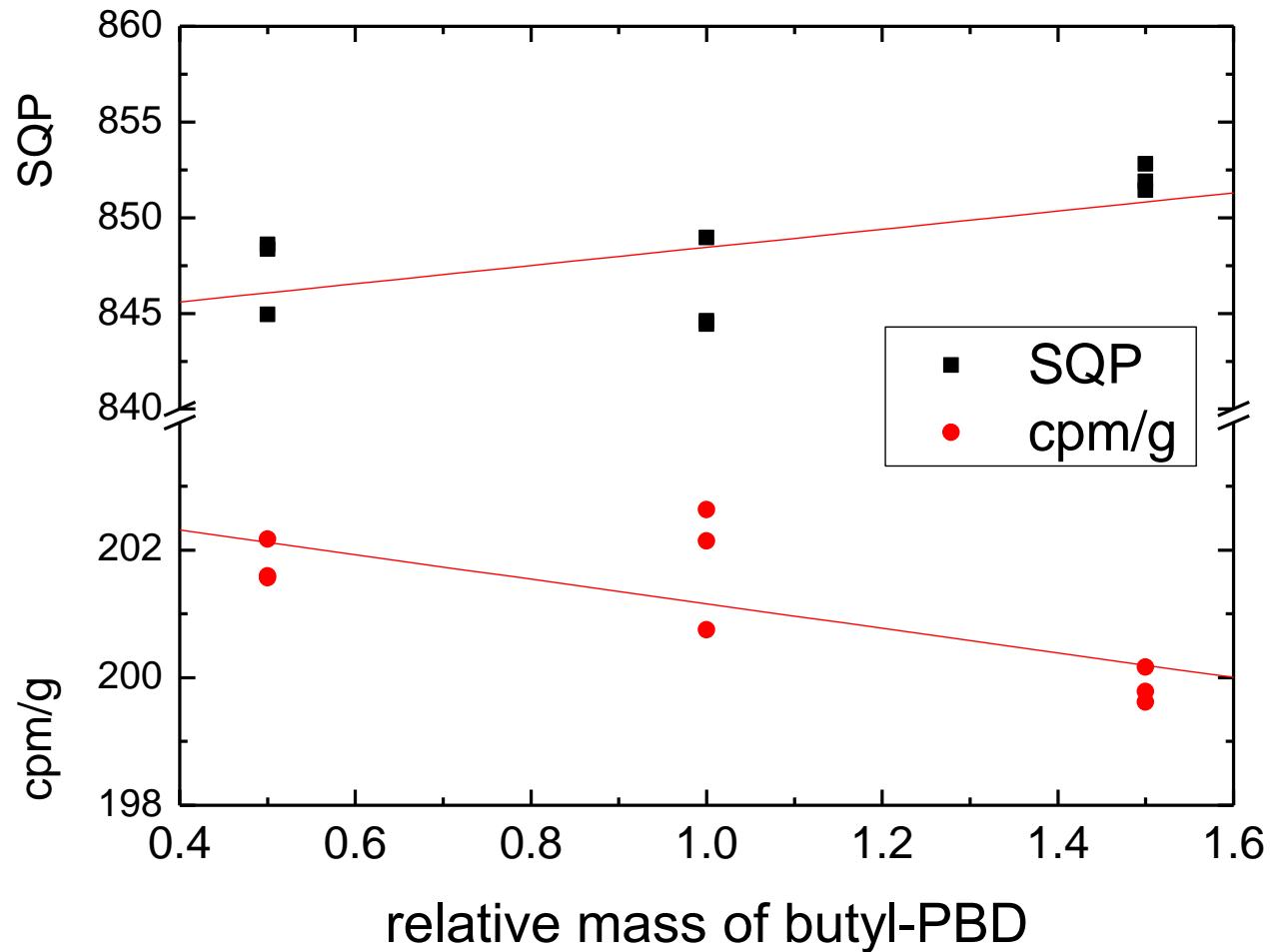


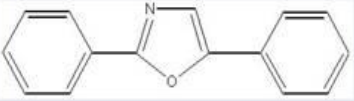
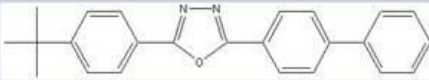



Validation of the method LSC-B



Mass of butyl-PBD is not critical



Primary Scintillators		
Scintillator	Molecular structure	Emission wavelength
PPO		357 nm
Butyl-PBD		363 nm
p-Terphenyl		340 nm

Recommendation

12 – 17 mg PDB per 1 g benzene

Relative mass = 1 → 15 mg/g

CO₂ absorption

Simple preparation

Good for relatively high ¹⁴C activities

Low amount of carbon absorbed

(max 0.7 g C in 10 mL Carbosorb)

Low sensitivity and precision

Benzene synthesis

Benzene is an ideal counting medium

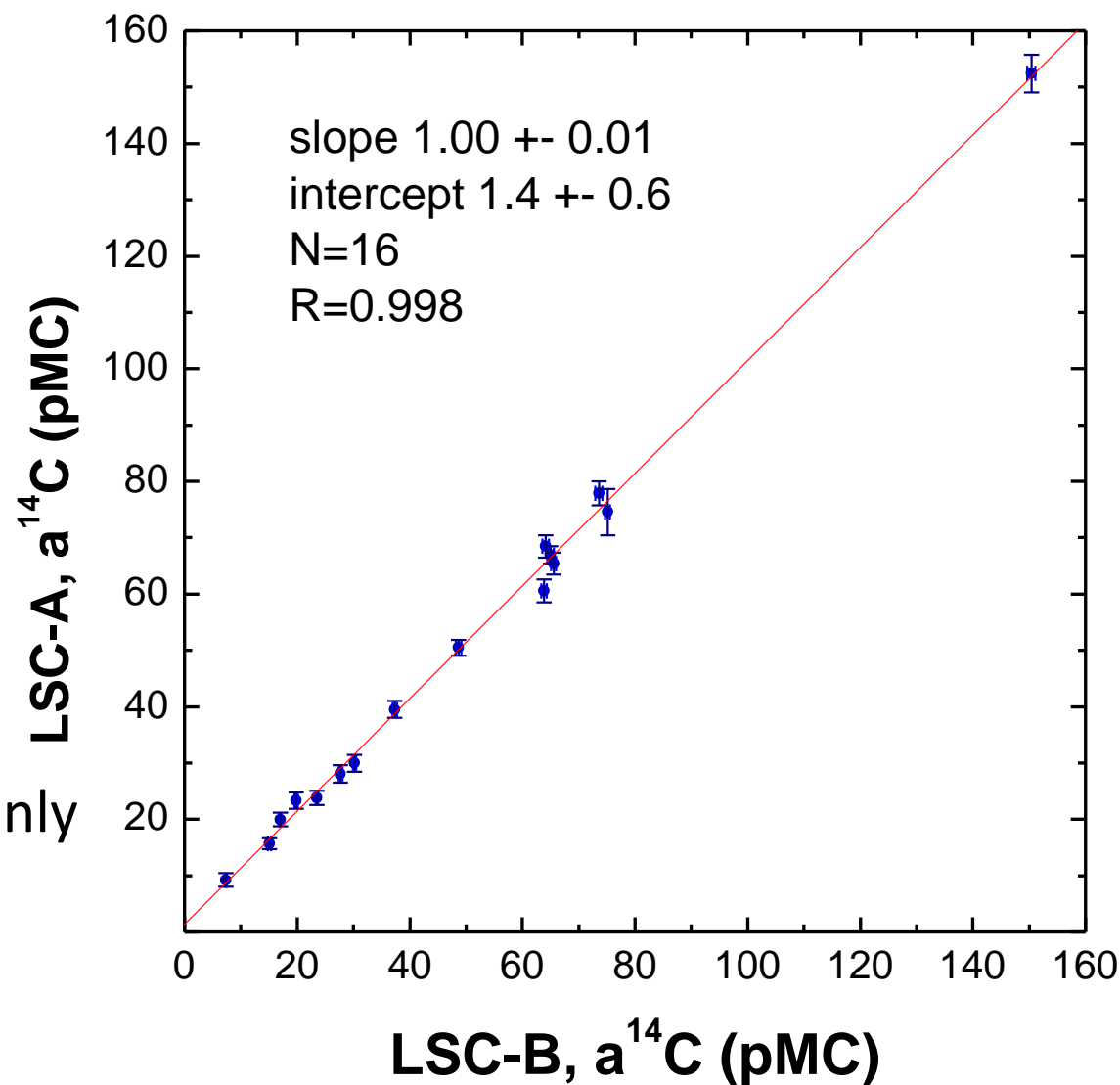
It has a high carbon content (92.3 %)

Synthesis relatively simple (!)

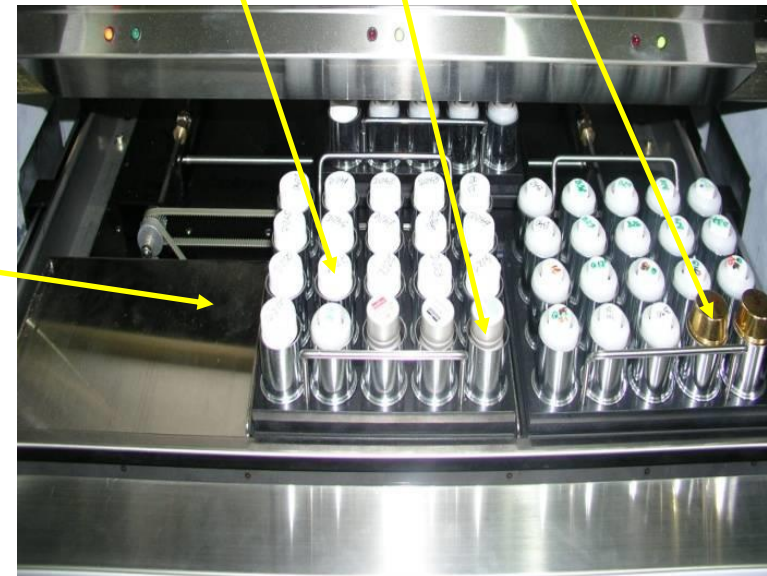
No requirement for a scintillation cocktail, only scintillator is added (Butyl-PBD, 12 – 15 mg per gram of benzene)





Reasonable resistance to quenching

Safety - cancerogenic



Liquid Scintillation Counting, Quantulus 1220

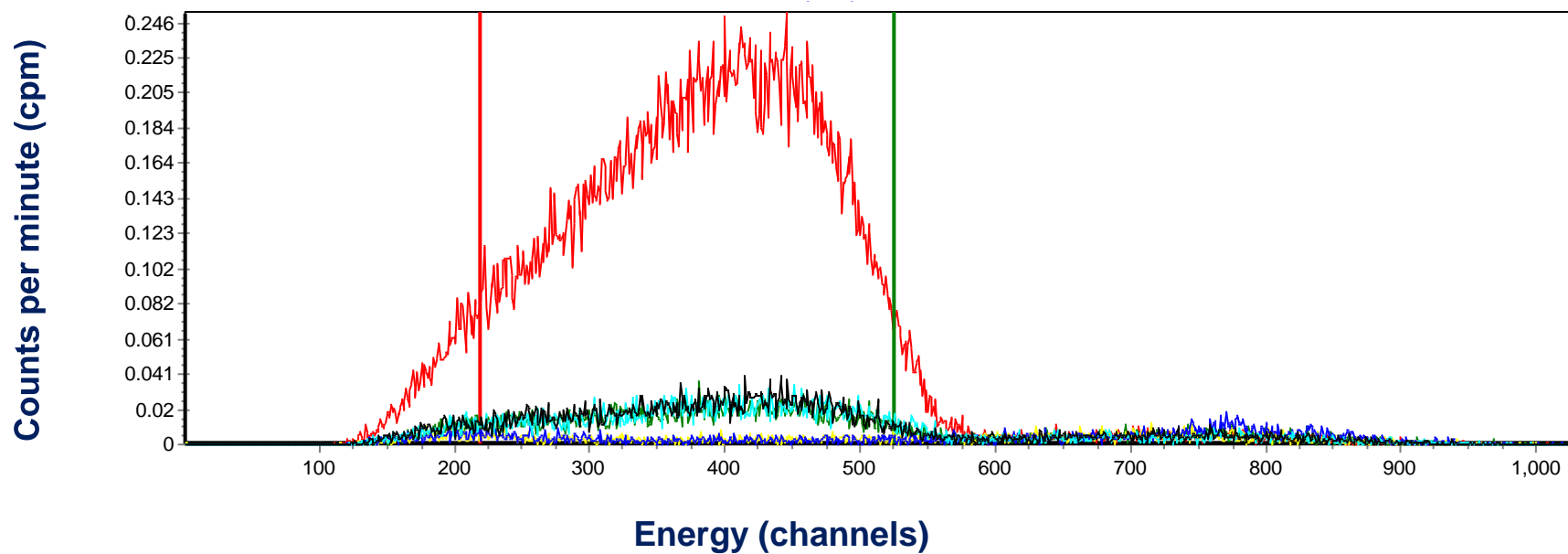
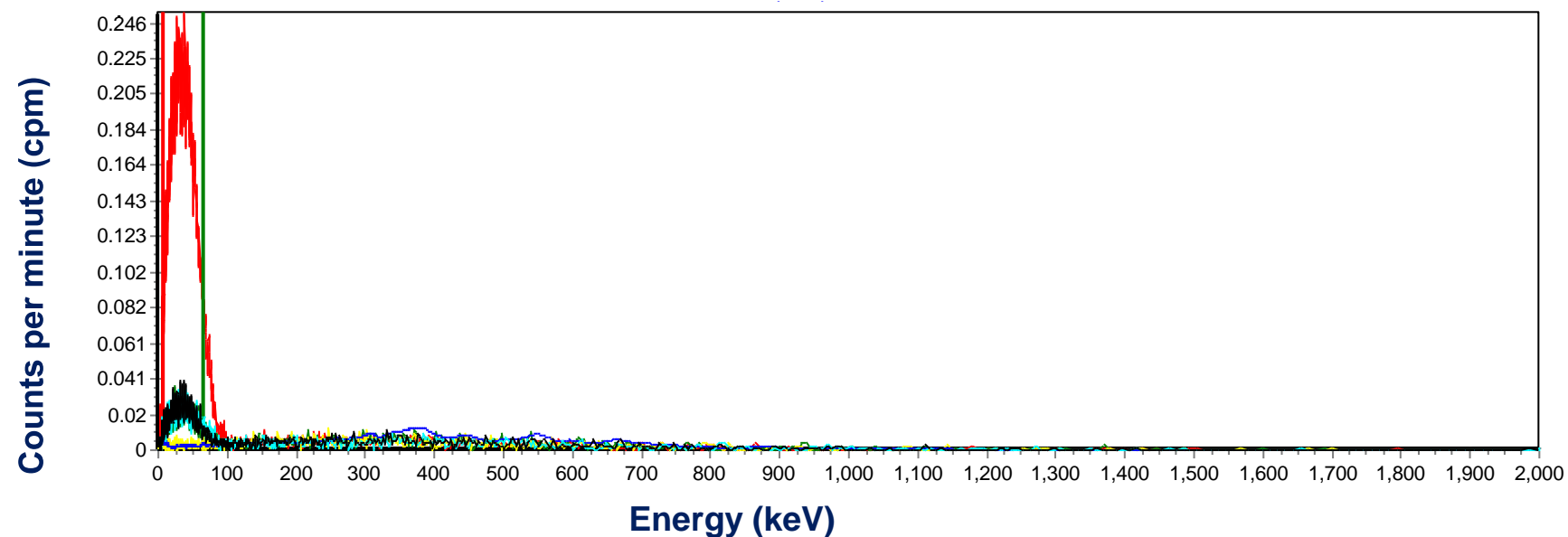


Benzene, C ₆ H ₆			Absorption CO ₂
			
Vial 7 mL, Glass Routine, 4 g	Vial 7 mL, Teflon copper High precision 4 g	Vial 3 mL, Teflon 2 g	Vial 20 mL, glass 2.2 g CO ₂
15 mg (Butyl-PBD) / 1g (benzene)			<i>Carbosorb</i> 10 mL + <i>Permafluor</i> 10 mL

**All samples in measured batch – same geometry, dilute if necessary
(inactive benzen)**

Dilution factor = m(sample + inactive benzene) / m (benzene sample)

^{14}C spectra
in LSC
Quantulus
1220



Optimization

Mesurement efficiency, E

Figure of merit, FM

Active radiocarbon standard, known activity, known dpm (exact mass of carbon in measured sample)!

$$E = A_{\text{measured}} (\text{cpm}) / A (\text{dpm})$$

$$F = A_{\text{measured}} / B^{1/2}$$

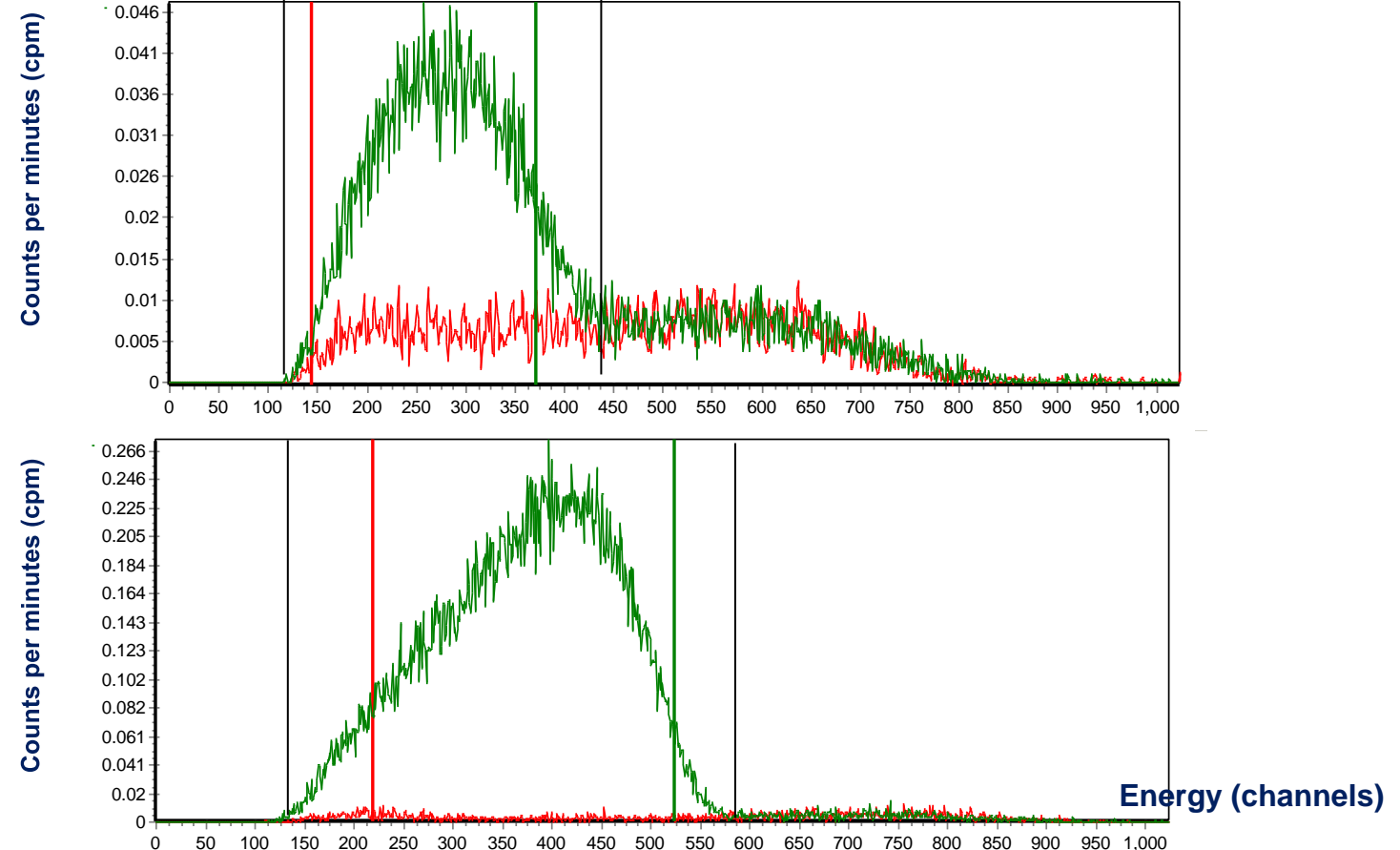
Counting window, ROI

LSC-A

LSC-A	¹⁴ C w.	working w.
B	2.4	1.80 (75%)
A	5.2	4.75 (92%)

LSC-B

LSC-B	¹⁴ C w.	working w.
B	1.34	0.87 (65%)
A	43.0	40.00 (93%)



LSC-A

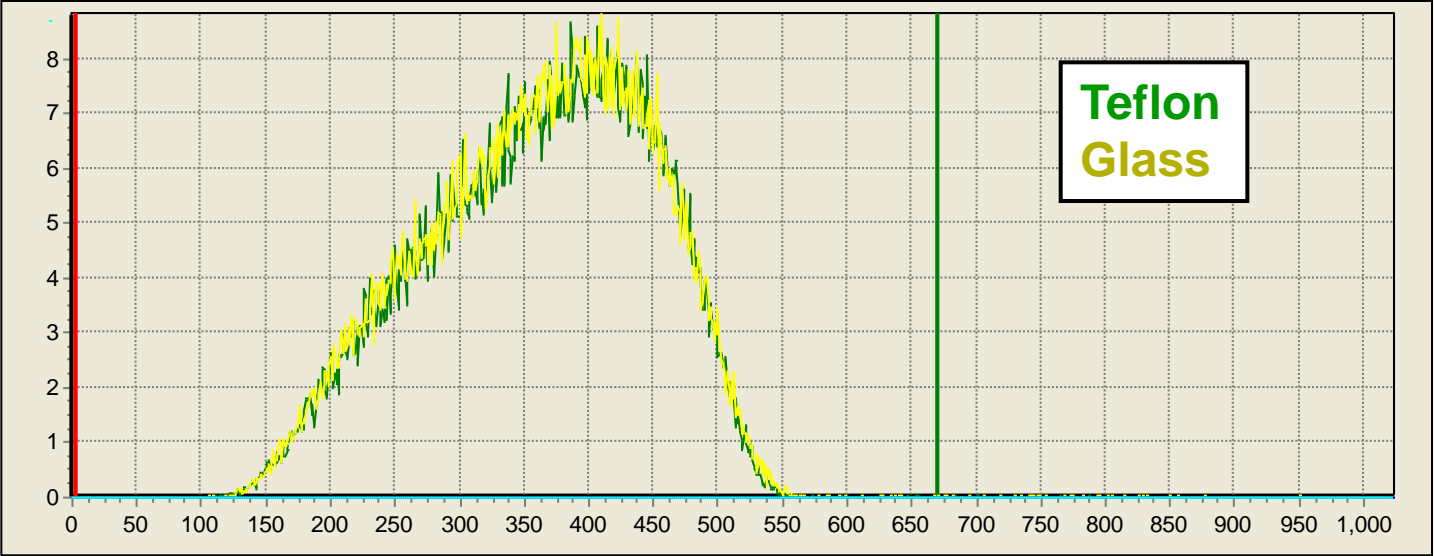
Measurand	Mark	Unit	¹⁴ C window	Count w. Region of int. (ROI)
Spectrum area		channel	109-431	144-372
Standard activity	<i>A</i>	dpm	7.98	7.98
Measured activity of standard	<i>A_m</i>	cpm	5.59	5.20
¹⁴ C spectrum share		%	100	93
Efficiency	<i>E</i>	%	70	65
Bacground count rate	<i>B</i>	cpm	1.95	1.47
Background share		%	100	75
Figure of merit	<i>FM</i>		16.0	18.4

LSC-B

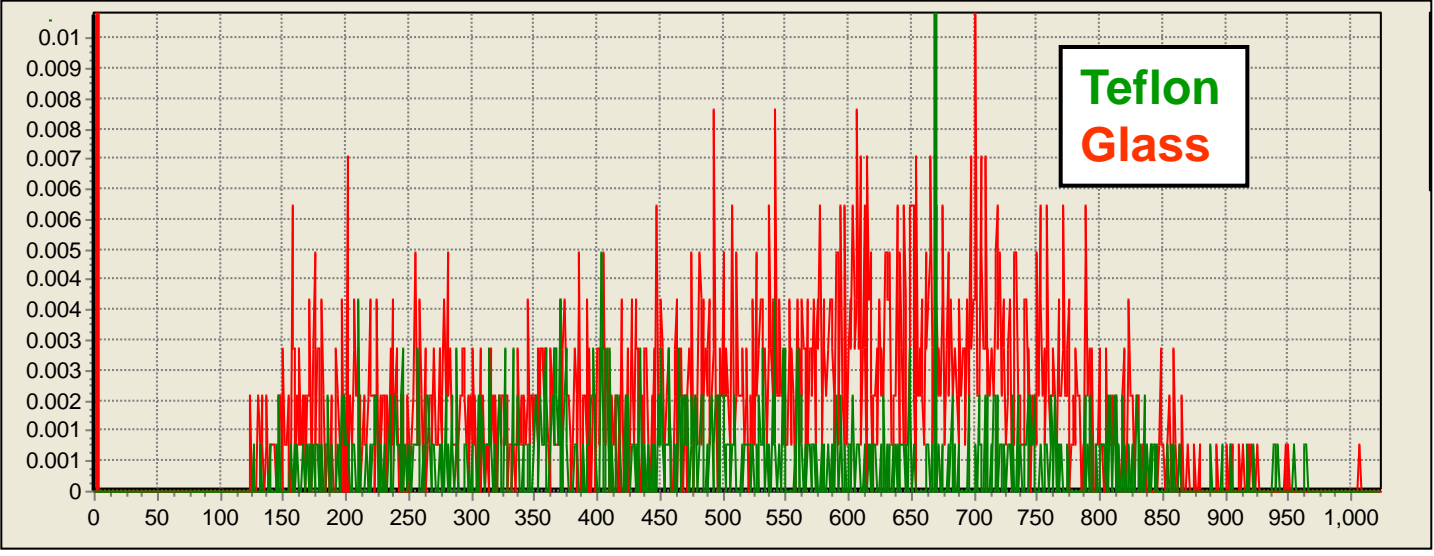
¹⁴ C window	Count w. Region of int. (ROI)
127-580	219-525
61.06	61.06
54.95	50.30
100	92
90	82
1.37	0,87
100	63
2200	2908

^{14}C spectra of and active sample and a background in two types of vials, 4 mL

Counts per minute (cpm)



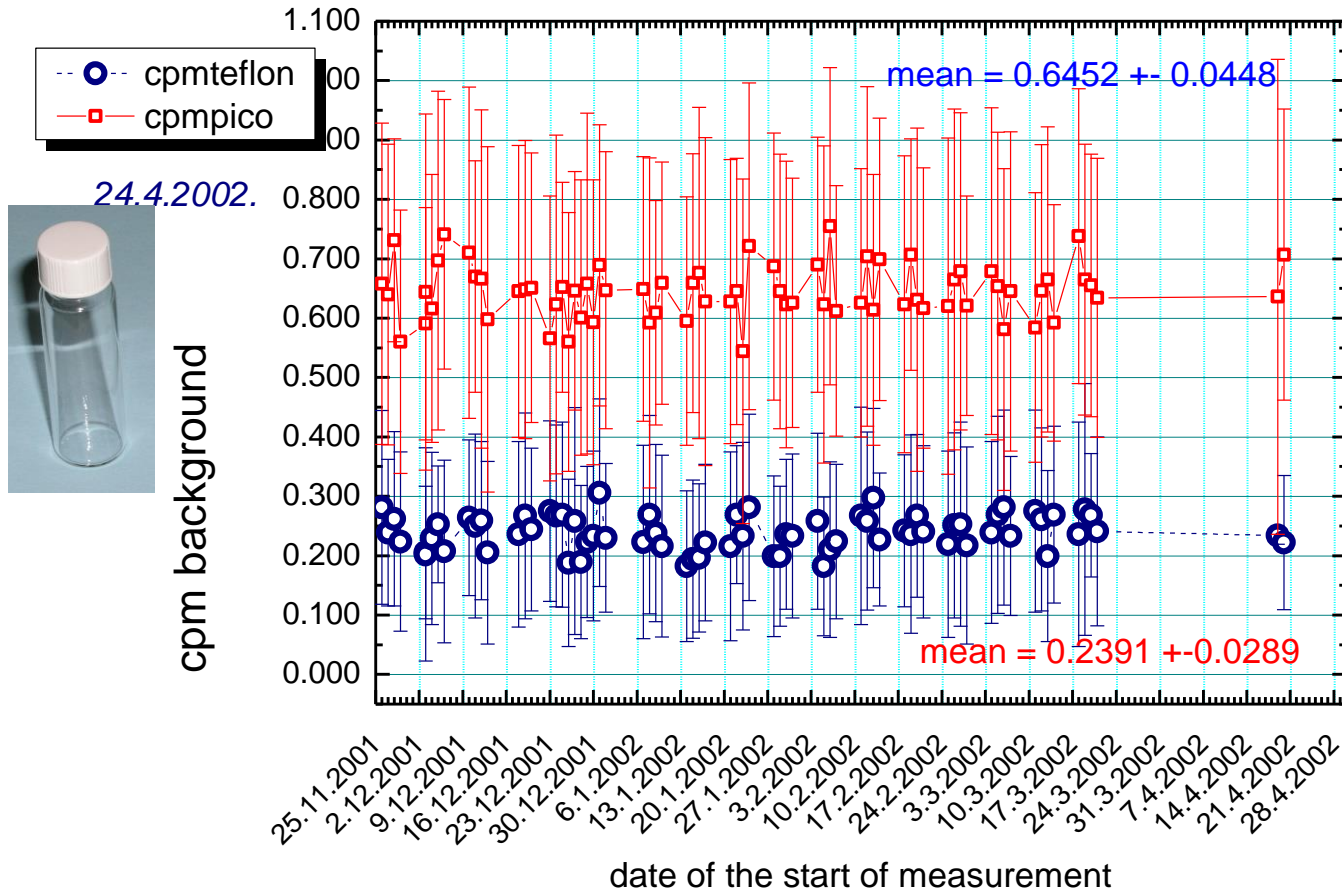
Counts per minute (cpm)



Energy (channels)

In addition, teflon-copper vials (7 mL) and Teflon black vials (3 mL) are available

Supposed to be cleaned and re-used, possible cross-contamination, careful cleaning needed, occasional tests



cpm backg. „black”
 $0.17 \pm 0.01 \text{ min}^{-1}$

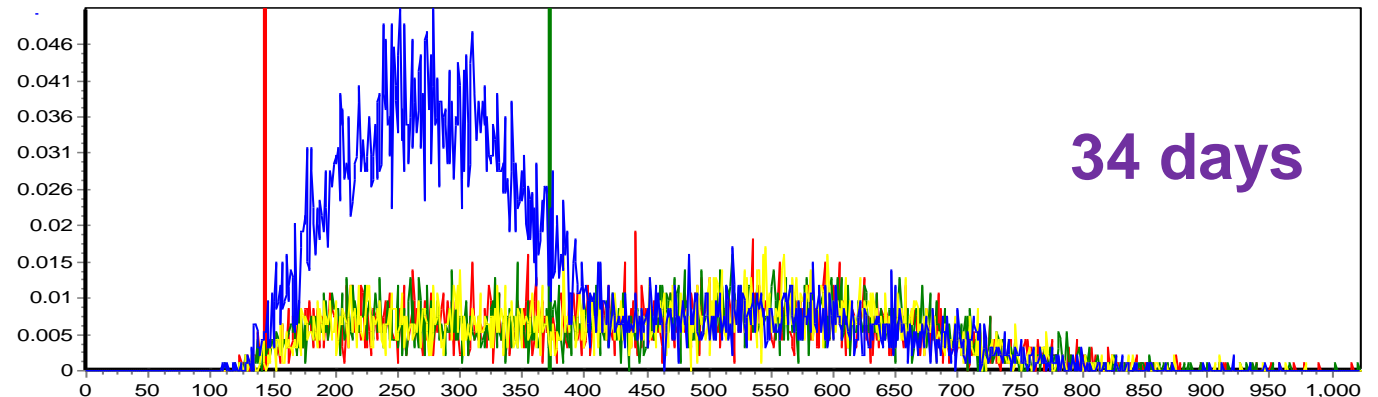
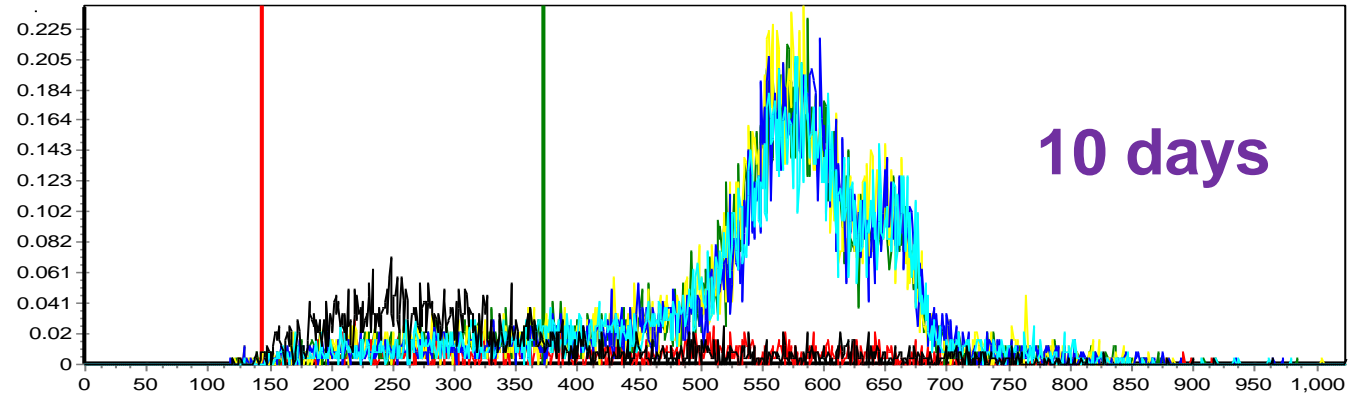
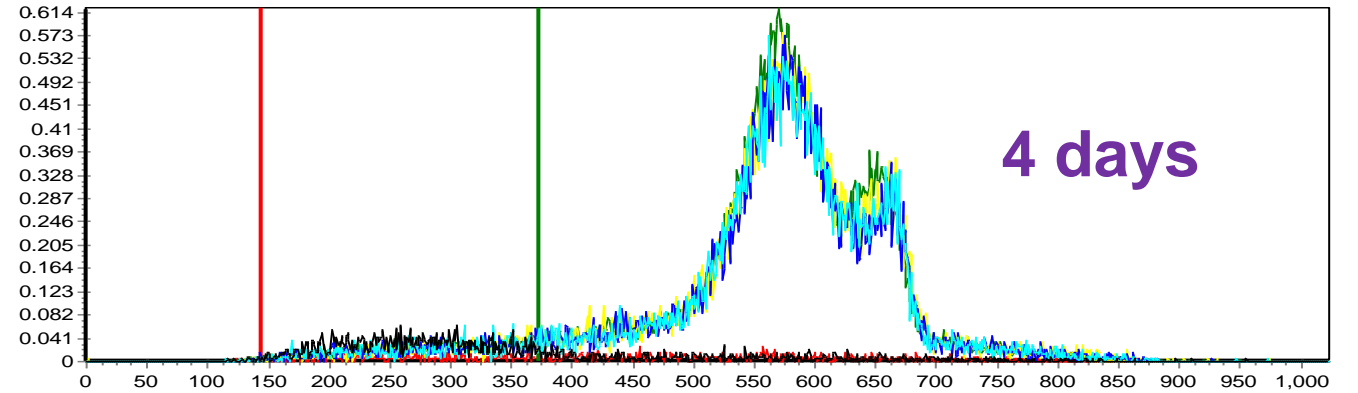
LSC measurement



Value	Symbol (unit)	LSC-A	LSC-B	LSC-B	LSC-B
Measured compound and its quantity	m (g)	CO ₂ , 2.2 g	benzene, 4 g	benzene, 4 g	benzene, 2 g
Amount of carbon	m (g)	0.6	3.7	3.7	1.85
Spectrum area (counting window)	(channel)	144—372	219—525	219—525	219—525
Real activity of standard ($a^{14}\text{C}=100$ pMC)	A (dpm)	7.99	50.07	50.07	25.03
Count rate of background	B (cpm)	1.80	0.87	0.21	0.16
Net count rate of standard ($a^{14}\text{C} = 100$ pMC)	A_{meas} (cpm)	4.75	40.0	40.5	16.0
Efficiency	(%)	60	80	81	64
Relative Factor of Merit (Gupta and Polach, 1985)		3.5	42.9	88.4	39.9
Maximum age ($t_{meas}=1200$ min)	T_{max}^*	30,300	50,300	56,000	49,800

Radon contributing to background

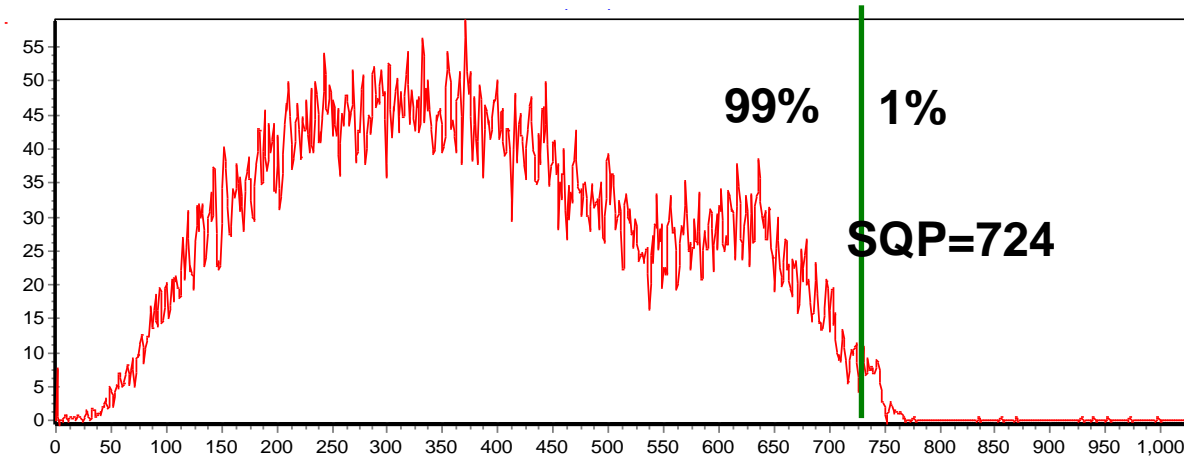
- Radon in air
- Radon in samples
- Radon in chemicals



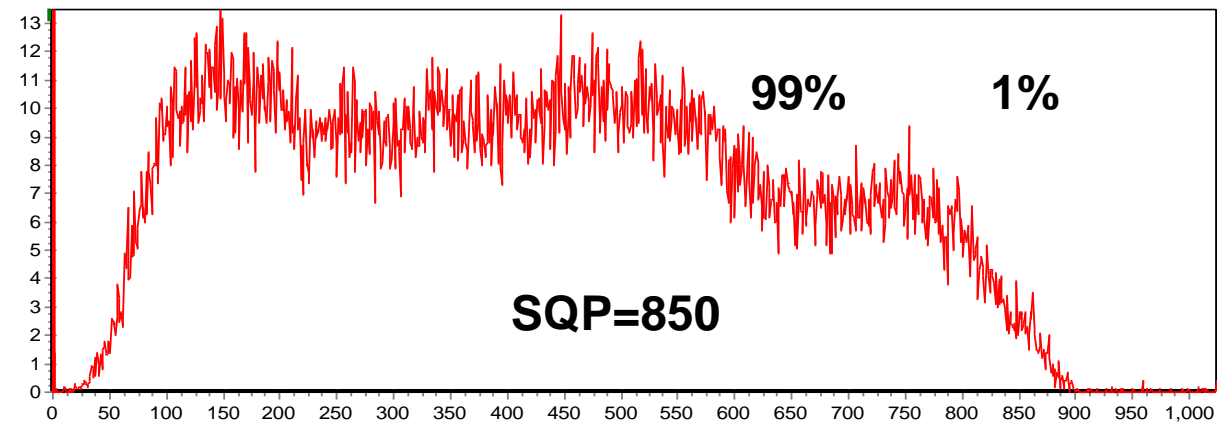
Quenching

SQP – Standard Quenching Parameter, measured for each sample, each cycle

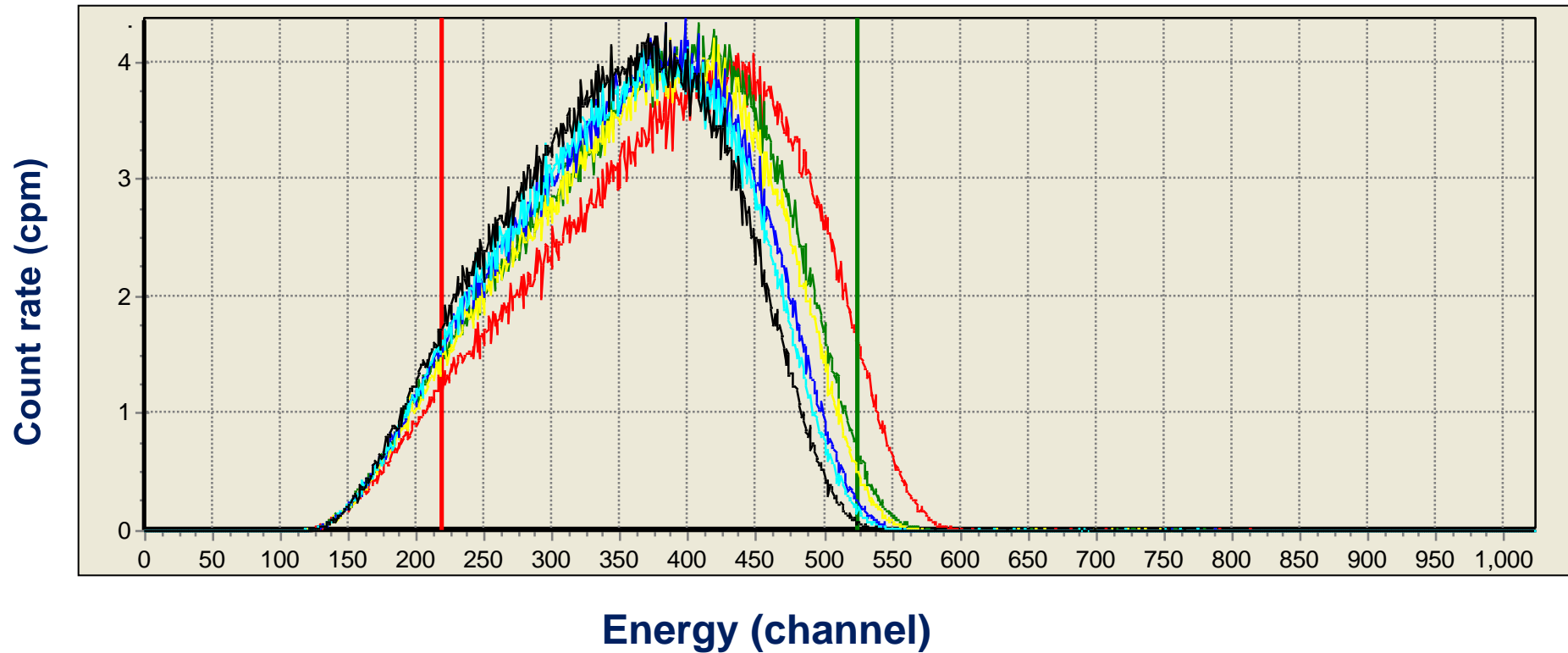
LSC-A



LSC-B



Quenching

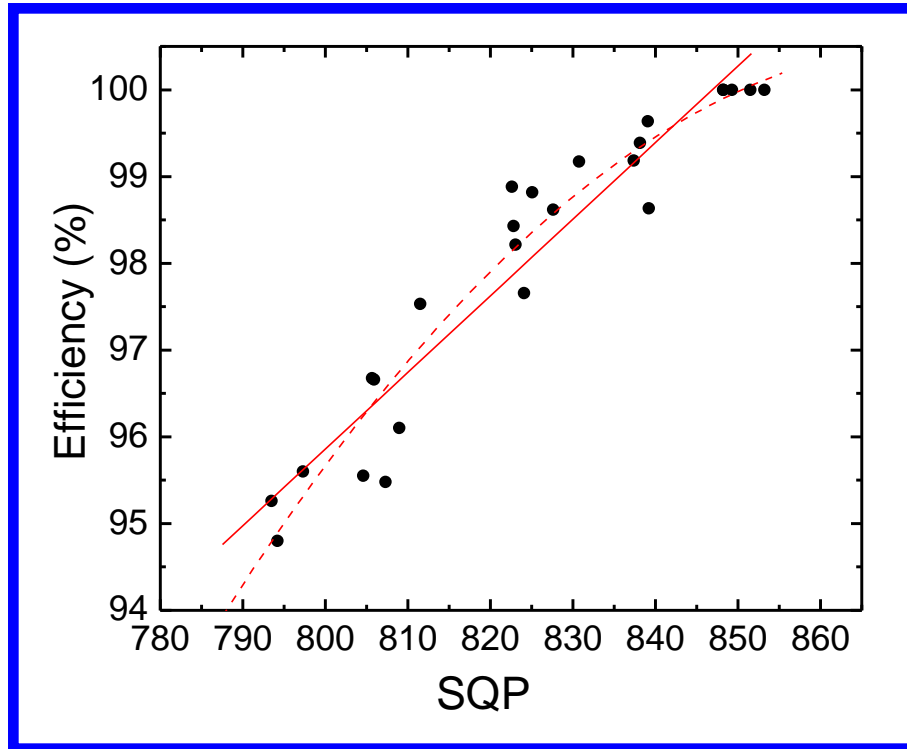


Quenched spectra are moved towards lower energies due to impurities (benzene samples)

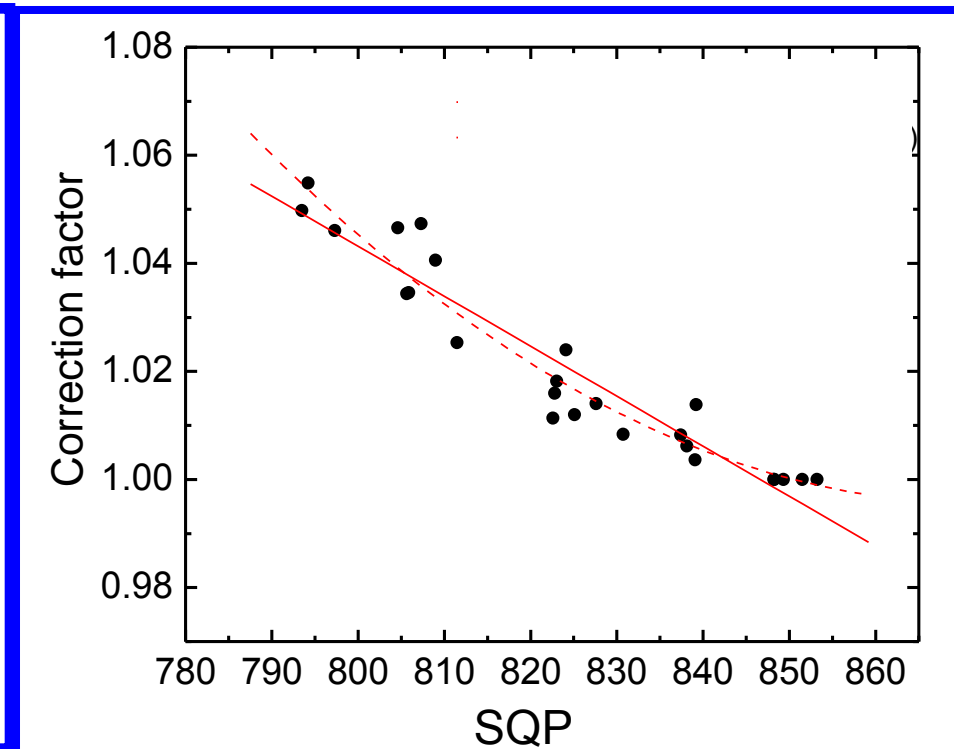
Measurement of benzene samples: high activity, same activity,
successive adding of „poison” (acetone diluted in benzene)

$$\text{Efficiency} = \text{cpm}_{\text{poisoned}} / \text{cpm}_{\text{clean}}$$

$$\text{Correction factor} = 1 / E$$



Quenching curve



Correction curve

Used referent material:

- Primary standard: OxalicAcid II (NIST)
- Secondary standard: Shells (Adriatic Sea)
- Control sample ANU Sucrose
- Backgrounds: Carrara marble
CO₂ – borehole gas
anthracite

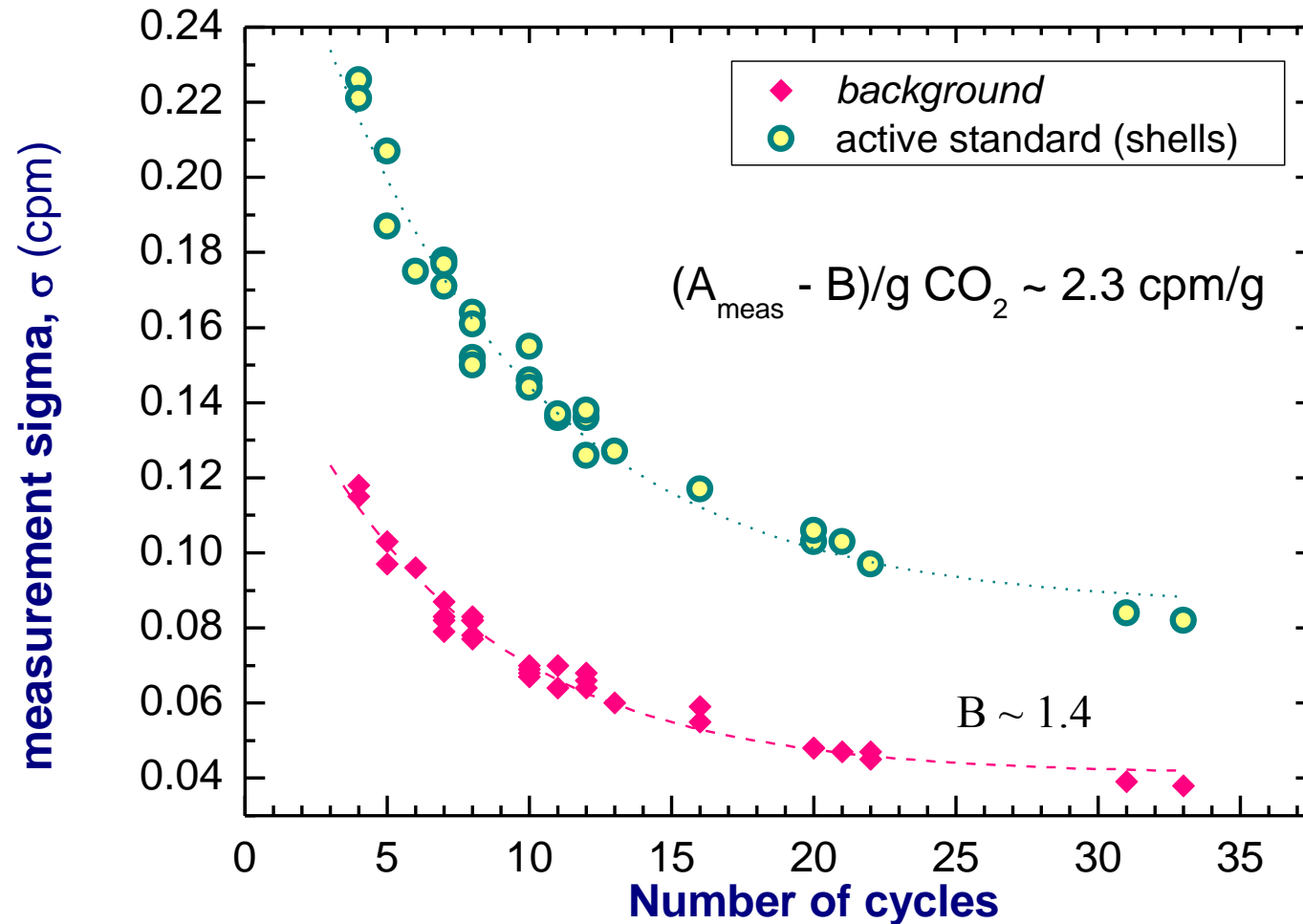
Measurement procedure

(quasi-simultaneous measurement)

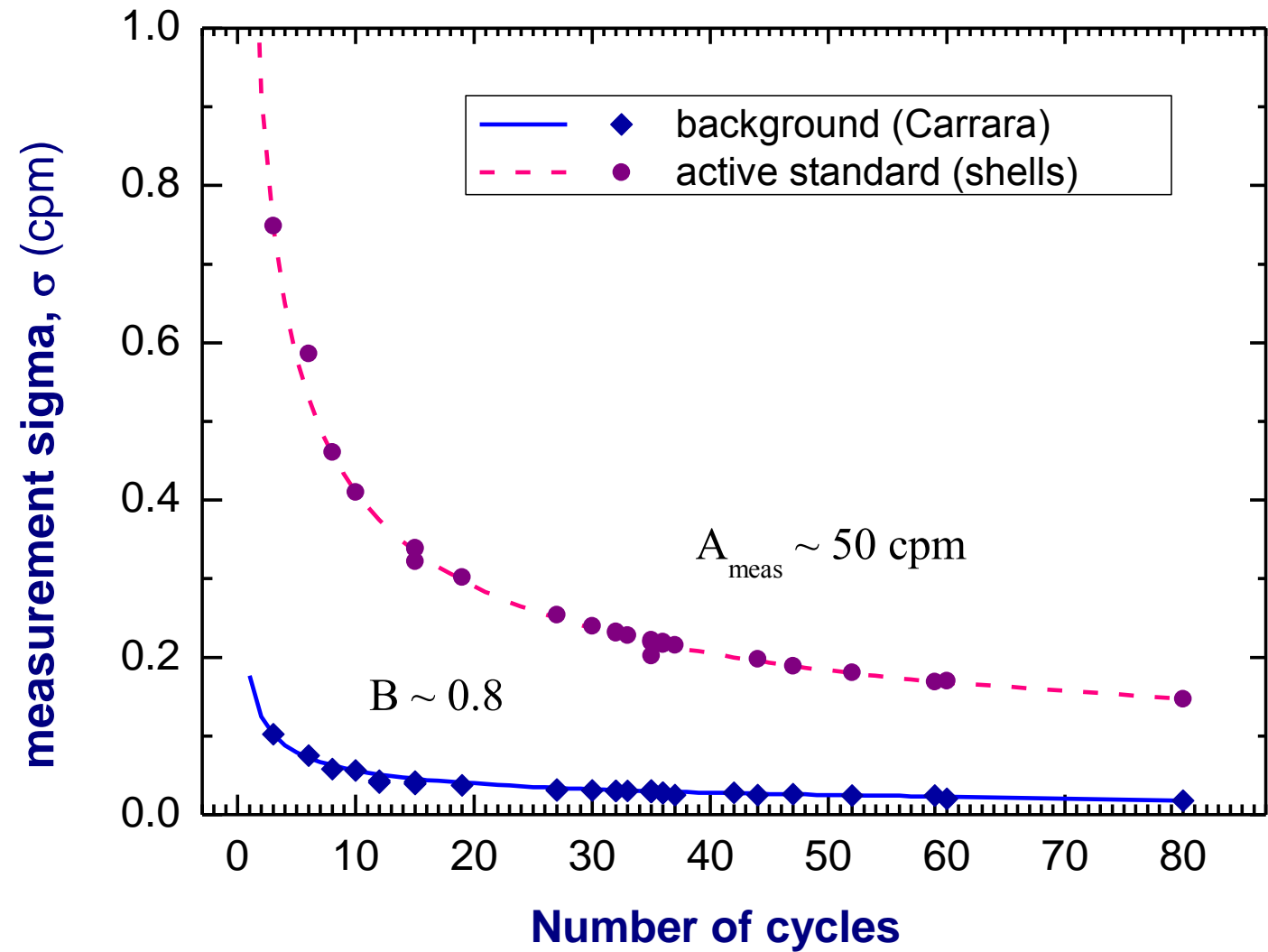
**LSC-A – 20 cycles, 30 min, all samples in duplicate, 2 backgrounds
2 second. standards (shells), 2 control samples
standard, RSD = 11.8%
background, RSD = 2.9%**

**LSC-B – 40 cycles, 30 min, 1 backgrounds, 1 primary standard, 2 control
standard, RSD = 0.3%
background, RSD = 1.8%**

Influence on the number of cycles (time of measurement) on standard deviation of measured count rates, **LSC-A**



LSC-B



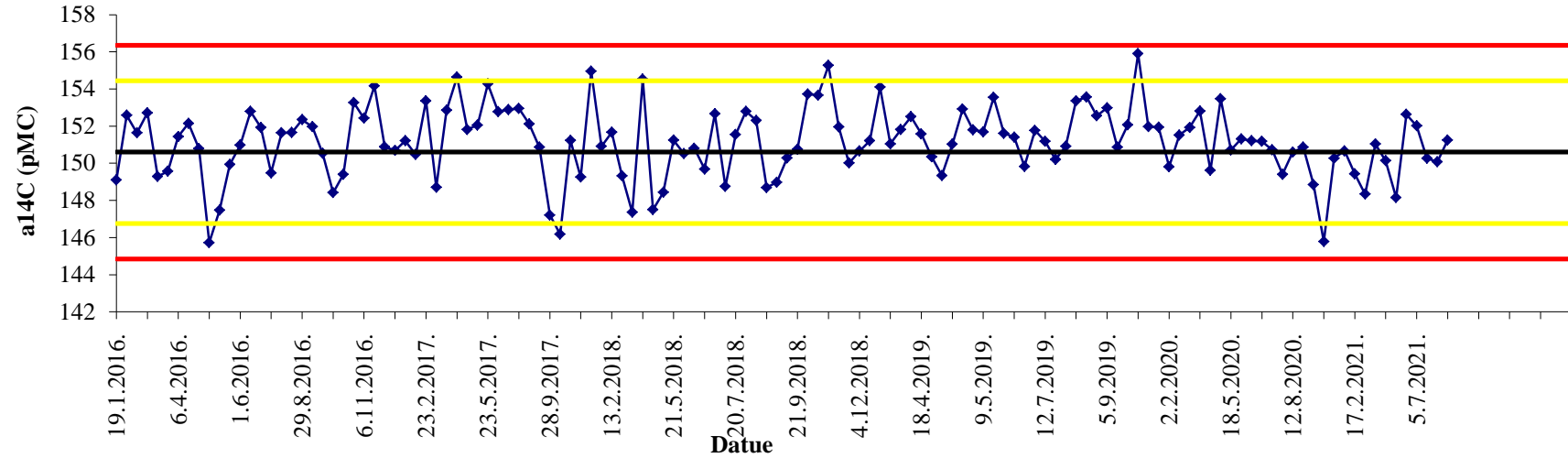
Result processing

										Nagib pravca		Odsječak											
Ime mjerne grupe (run):					Benzen 15-2021			Korekcija za masu uzorka bez analita:		0.0779 ± 0.0046													
Datum početka mjerenja:					19.08.21.			Korekcija zbog gašenja (Quench correction):		0.0844 ± 0.0075		28.53											
Datum završetka mjerenja:					27.08.21.																		
Broj ciklusa:					10			Aktivnost ¹⁴ C standarda (a ¹⁴ C u 1950.):		134.07 (pMC)				Neto odbroj C _{net} za 100 pMC po g: 9.714									
No.	Lab. broj Z-	Bbroj pripreme	Naziv uzorka	Broj 30-min intervala	Datum uzorkovanja	Datum pripreme	m CO ₂ (g)	P (m _{sed} /m _{sed})	SQP	C (min ⁻¹) "Average" "Error"	δ ¹³ C	A ₀	C Rn	Napomena	C _{net} /m min ⁻¹ g ⁻¹	Rezultat a ¹⁴ C (pMC)	Konvencijska starost (BP)	Konačni rezultat (zaokružen)					
B	1000	B1210	Antracit	40	01.01.60.	13.05.15.	4.2213	1.000	838.0	0.930 ± 0.028	-25.0 ± 0.1	100	0.56		0.222		uzorak bez analita	Konvencijska starost (BP)					
S	3500	B1711	Oxalic acid II	40	15.07.83.	10.06.20.	4.1802	1.000	850.7	55.373 ± 0.216	-17.8 ± 0.1	100	0.81		12.987		referentni standard	ili a ¹⁴ C, ako a ¹⁴ C >100 pM					
1	3000	B1317	ANU Saharoza 150.6 pMC	20	01.01.60.	19.02.16.	4.1689	1.000	841.4	62.044 ± 0.324	-11.2 ± 0.1	100	0.83	OK	14.733	150.08 ± 1.00	Modern ± --	150.1	1				
2	4300	B1065	Školjke-Zadar 101 PMC	20	01.03.09.	25.07.13.	3.6323	1.000	824.8	37.086 ± 0.250	0.0 ± 0.1	100	0.5	OK	10.147	101.06 ± 0.81	Modern ± --	101.1	0.8				
3	7594	B1785	Atm CO2 G Jelenje 2/2021	40	01.03.21.	21.05.21.	4.2047	1.328	841.3	31.106 ± 0.162	-24.0 ± 0.1	100	0.86	benz11, 102.1 +- 0.7 pMC	9.877	100.17 ± 0.68	Modern ± --	100.2	0.7				
4	7675	B1800	Atm CO2 Parg 4/2021	40	01.05.21.	30.07.21.	3.8080	1.000	843.3	37.434 ± 0.178	-24.0 ± 0.1	100	0.76		9.864	100.59 ± 0.64	Modern ± --	100.6	0.6				
5	7717	B1801	Atm CO2 Zagreb IRB 7/2021	40	31.07.21.	04.08.21.	4.2330	1.459	844.6	27.471 ± 0.155	-24.0 ± 0.1	100	0.9		9.488	95.82 ± 0.69	343 ± 58	340	60				
6	7676	B1802	Atm CO2 Rijeka 5/2021	40	01.06.21.	11.08.21.	4.0503	1.515	848.1	26.383 ± 0.149	-24.0 ± 0.1	100	0.8		9.862	99.48 ± 0.71	42 ± --	Nije definirano	Nije defini				
7	7677	B1803	Atm CO2 G Jelenje 5/2021	40	01.06.21.	13.08.21.	4.0803	1.000	852.7	39.893 ± 0.188	-24.0 ± 0.1	100	1.1		9.770	99.37 ± 0.63	51 ± 51	50	50				
8	7678	B1804	Atm CO2 Parg 5/2021	40	01.06.21.	18.08.21.	3.8597	1.000	839.6	37.524 ± 0.178	-24.0 ± 0.1	100	1.0		9.715	99.80 ± 0.63	16 ± --	Nije definirano	Nije defini				
9										±	0.0 ± 0.1	100	0.8			-- ± --	-- ± --	-	-				
10										±	0.0 ± 0.1	100	0.8			-- ± --	-- ± --	-	-				
11										±	0.0 ± 0.1	100	0.8			-- ± --	-- ± --	-	-				
12										±	0.0 ± 0.1	100	0.9			-- ± --	-- ± --	-	-				
13										±	0.0 ± 0.1	100	0.9			-- ± --	-- ± --	-	-				
14										±	0.0 ± 0.1	100	0.8			-- ± --	-- ± --	-	-				
15										±	0.0 ± 0.1	100	0.8			-- ± --	-- ± --	-	-				
16										±	±					-- ± --	-- ± --	-	-				
17										±	±					-- ± --	-- ± --	-	-				
18										±	±					-- ± --	-- ± --	-	-				
19										±	±					-- ± --	-- ± --	-	-				
20										±	±					-- ± --	-- ± --	-	-				
					t _{min} (years)	t _{max} (years)	δ _{min} (‰)	a ¹⁴ C _{min} (pMC)					Obradio/la:	ikb 30.8.2021.									
					61	46126	-996.8	0.32															
Protokol					Benzen15		Izradio:	as	Pregledao:		ikb		Pregledao/la:										
Napomena uz mierenie:																							

		Sample name: Z-		Sample No. 4								
Run name:	Benzen_14-2021		7673		B1796							
Start:	28.07.21.		Atm CO2 Rijeka 4/2021									
End:	05.08.21.											
No.of cycles:	10		Sample preparation date		28.07.21.							
STANDARDS INPUT DATA			QUENCH CORRECTIONS									
Background sample mass (mB)		4.223	Background quench corr.		0.987	Result		Error				
Background count rate (Bo)		0.890	Mod.std. quench corr.		1.006							
Background count rate error (σBo)		0.028	Sample quench corr.		1.000							
SQP background		832.4										
Activity of mod.standard (A)		134.1										
Mod. Standard sample mass (mS)		4.1823										
Mod.standard count rate (S)		55.032										
Mod.standard count rate error (σS)		0.215										
Delta ¹³ C od std. (δ ¹³ C)		-17.80										
Delta ¹³ C of std. error (σ[δ ¹³ C])		0.10										
SQP modern standard		854.2										
SAMPLE INPUT DATA			RESULTS									
Sample code		B1796	% mod		97.42	Result		Error				
Sample preparation date		28.07.2021	% mod (δ13C corr.)		98.65			0.62				
Benzene weight (mC)		4.0489	Abs % mod		96.59							
Weight ratio (W _{tot} /W _{net})		1	δ ¹³ C		-24.00			0.10				
Sample count rate (CPM)		38.765	δ ¹⁴ C		-25.77			6.12				
Sample count rate error (σCPM)		0.181	Δ ¹⁴ C		-13.51			6.20				
Delta ¹³ C (δ ¹³ C)		-24.00	σ1		51							
Delta ¹³ C error (σ[δ ¹³ C])		0.10	Conventional age (mean)		109 years BP							
A ₀		100	σ2		50							
SQP sample		847.7	Age (A ₀ correction)		109							
Comment:	0		Control:									

	Slope (±σ)		Intercept (±σ)
B.correct.:	0.0779	0.0046	
Q.correct.:	0.0844	0.0075	28.530 ± #REF!
B	0.888	Backg. corr. on sample weight	
σ(B)	0.028	Corr. background error	
Sn	40.146	Net mod.standard counts	
σ(Sn)	0.161	Net mod.standard counts error	
SnCorr	39.568	Net mod. std. cts. 13C corr.	
σ(SnCorr)	0.159	Net mod. str. cts. error 13C corr.	
Cn	39.112	Net san ± e counts	
σ(Cn)	0.189	Net sample counts error	
CnCorr	39.034	Net sample ± s. 13C corr.	
σ(CnCorr)	0.189	Net sample cts. error 13C corr.	
δ14C	-25.767	Delta value	
σ(δ14C)	6.119	Delta value error	
Δ14C	-13.510	Delta value corrected for 13C	
s(Δ14C)	6.196	Delta value corrected error	
pMC	97.423	% modern carbon	
σ(pMC)	0.612	% modern carbon error	
pMC corr.	98.649	% modern carbon	
σ(pMC) corr.	0.620	% modern carbon error	
AGE from now	109.26	Mid age	
σ1(age)	159.87	Age plus error	
σ2(age)	58.97	Age minus error	
DATE	1911.74	Today-Mid age	
σ1(date)	50.61	Age with error-mid age	
σ2(date)	50.29	Age with error+mid age	

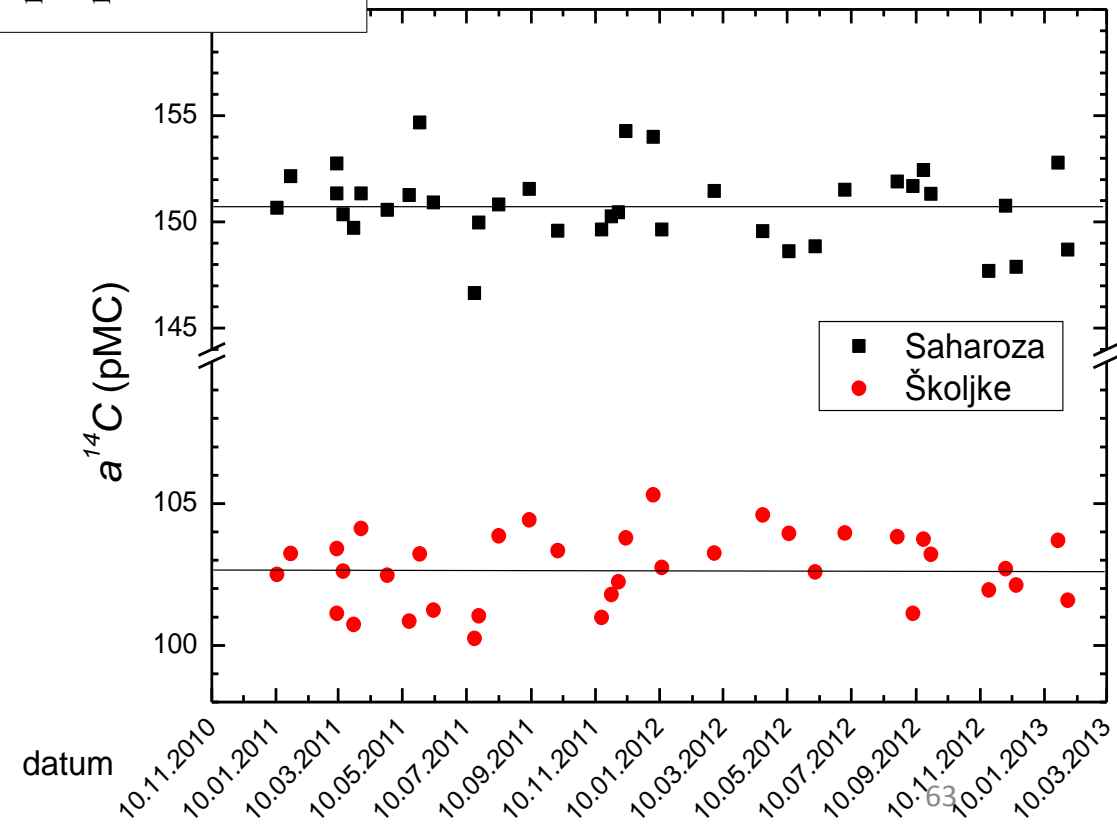
Run name: DirAbs_2-2021																		
Run start: 05.02.21.																		
Run end: 17.02.21.																		
No. of cycles: 20																		
Activity of standard: 100.1 (pMC)																		
Net CPM of 100 pMC per g: 1.989																		
No.	Lab. code Z-	Prep. code	Sample name	No.30min interval s	Collection date	Preparation date	m CO2 (n)	SQP	C (min-1) Average Error	δ13C	A0	C Rn	Comment	C/m min-1g-1	Result a14C (pMC)	Conventional Age (BP)	Final result rounded	
B	1500	D1917	Rogaška	40	20.01.00.	03.02.21.	2.2065	709.7	1.967 ± 0.041	-25.0 ± 0.1	100	1.3		0.891		Background	Conv. Age (BP)	
S	6118	D1919	Dagnje 4/16 Dubrovnik 100,1 +- 0,6 pMC	20	15.04.16.	03.02.21.	2.3103	704.1	6.566 ± 0.105	0.0 ± 0.1	100	1.4		2.842		Active standard	a14C if >100 pMC	
1	1500	D1918	Rogaška	40	01.01.60.	03.02.21.	2.0872	711.0	1.906 ± 0.040	-25.0 ± 0.1	100	1.4		0.913	-1.55 ± 1.45	Old ± --	#VALUE!	#VALUE!
2	6118	D1920	Dagnje 4/16 Dubrovnik 100,1 +- 0,6 pMC	20	15.04.16.	03.02.21.	2.1328	708.8	6.249 ± 0.103	0.0 ± 0.1	100	1.5		2.930	100.96 ± 3.60	Modern ± --	101	3.6
3	7127	D1921	NEK-2-2019, jabuka G490, 26.9.2019.	20	26.09.19.	03.02.21.	2.2406	705.8	6.432 ± 0.104	-27.0 ± 0.1	100	1.4		2.871	105.90 ± 3.71	Modern ± --	105.9	3.7
4	7127	D1922	NEK-2-2019, jabuka G490, 26.9.2019.	20	26.09.19.	03.02.21.	2.4381	695.1	6.833 ± 0.107	-27.0 ± 0.1	100	1.2		2.803	106.06 ± 3.61	Modern ± --	106.1	3.6
5	7381	D1923	NEK-2-2020, Jabuka R527, 22.9.2020.	20	22.09.20.	03.02.21.	2.2147	712.6	6.350 ± 0.103	-27.0 ± 0.1	100	1.7		2.867	105.17 ± 3.70	Modern ± --	105.2	3.7
6	7381	D1924	NEK-2-2020, Jabuka R527, 22.9.2020.	20	22.09.20.	03.02.21.	2.0966	711.1	6.244 ± 0.103	-27.0 ± 0.1	100	1.8		2.978	108.41 ± 3.87	Modern ± --	108.4	3.9
7	7382	D1925	NEK-2-2020, Jabuka I528, 22.9.2020.	20	22.09.20.	04.02.21.	2.0180	719.5	6.457 ± 0.104	-27.0 ± 0.1	100	2.0		3.200	118.24 ± 4.13	Modern ± --	118.2	4.1
8	7382	D1926	NEK-2-2020, Jabuka I528, 22.9.2020.	20	22.09.20.	04.02.21.	2.1585	717.5	6.506 ± 0.105	-27.0 ± 0.1	100	2.2		3.014	111.75 ± 3.90	Modern ± --	111.8	3.9
9	7383	D1927	NEK-2-2020, Jabuka J529, 22.9.2020.	20	22.09.20.	04.02.21.	2.2707	706.3	6.701 ± 0.106	-27.0 ± 0.1	100	1.6		2.951	110.79 ± 3.80	Modern ± --	110.8	3.8
10	7383	D1928	NEK-2-2020, Jabuka J529, 22.9.2020.	20	22.09.20.	04.02.21.	2.2999	711.6	6.607 ± 0.106	-27.0 ± 0.1	100	1.7		2.873	107.22 ± 3.72	Modern ± --	107.2	3.7
11	7384	D1929	NEK-2-2020, Kukuruz L530, 22.9.2020.	20	22.09.20.	04.02.21.	2.0952	711.8	6.622 ± 0.106	-12.0 ± 0.1	100	2.4		3.161	114.54 ± 3.96	Modern ± --	114.5	4
12	7384	D1930	NEK-2-2020, Kukuruz L530, 22.9.2020.	20	22.09.20.	04.02.21.	2.1309	710.8	6.305 ± 0.103	-12.0 ± 0.1	100	2.3		2.959	104.95 ± 3.72	Modern ± --	105	3.7
13	7385	D1931	NEK-2-2020, Kukuruz N531, 22.9.2020.	20	22.09.20.	04.02.21.	2.4246	706.0	6.922 ± 0.108	-12.0 ± 0.1	100	1.6		2.855	105.36 ± 3.56	Modern ± --	105.4	3.6
14	7385	D1932	NEK-2-2020, Kukuruz N531, 22.9.2020.	20	22.09.20.	04.02.21.	2.1663	707.5	6.479 ± 0.105	-12.0 ± 0.1	100	1.8		2.991	107.38 ± 3.76	Modern ± --	107.4	3.8
15	7386	D1933	NEK-2-2020, Kukuruz O532, 22.9.2020.	20	22.09.20.	05.02.21.	2.0375	707.2	6.504 ± 0.105	-12.0 ± 0.1	100	3.2		3.192	114.80 ± 4.01	Modern ± --	114.8	4
16	7386	D1934	NEK-2-2020, Kukuruz O532, 22.9.2020.	20	22.09.20.	05.02.21.	2.1678	708.3	6.487 ± 0.105	-12.0 ± 0.1	100	2.7		2.992	107.50 ± 3.76	Modern ± --	107.5	3.8
17	7387	D1935	NEK-2-2020, Kukuruz Dob533, 22.9.2020	20	22.09.20.	05.02.21.	2.0082	708.2	6.435 ± 0.104	-12.0 ± 0.1	100	4.0		3.204	114.70 ± 4.02	Modern ± --	114.7	4
18	7387	D1936	NEK-2-2020, Kukuruz Dob533, 22.9.2020	20	22.09.20.	05.02.21.	2.2545	713.5	6.769 ± 0.107	-12.0 ± 0.1	100	3.0		3.002	109.81 ± 3.76	Modern ± --	109.8	3.8
19	7388	D1937	NEK-2-2020, Kukuruz 534, 22.9.2020.	20	22.09.20.	05.02.21.	2.0532	721.2	6.713 ± 0.106	-12.0 ± 0.1	100	4.5		3.270	119.17 ± 4.08	Modern ± --	119.2	4.1
20	7388	D1938	NEK-2-2020, Kukuruz 534, 22.9.2020.	20	22.09.20.	05.02.21.	2.2019	718.2	6.875 ± 0.108	-12.0 ± 0.1	100	3.3		3.122	114.92 ± 3.91	Modern ± --	114.9	3.9
21	7389	D1939	NEK-2-2020, Kukuruz H535, 22.9.2020.	20	22.09.20.	05.02.21.	2.0222		±	-12.0 ± 0.1	100			0.000	-50.15 ± 1.61	Old ± --	#VALUE!	#VALUE!
22	7389	D1940	NEK-2-2020, Kukuruz H535, 22.9.2020.	20	22.09.20.	05.02.21.	2.2402	712.1	6.960 ± 0.077	-12.0 ± 0.1	100	3.0		3.107	114.91 ± 3.46	Modern ± --	114.9	3.5



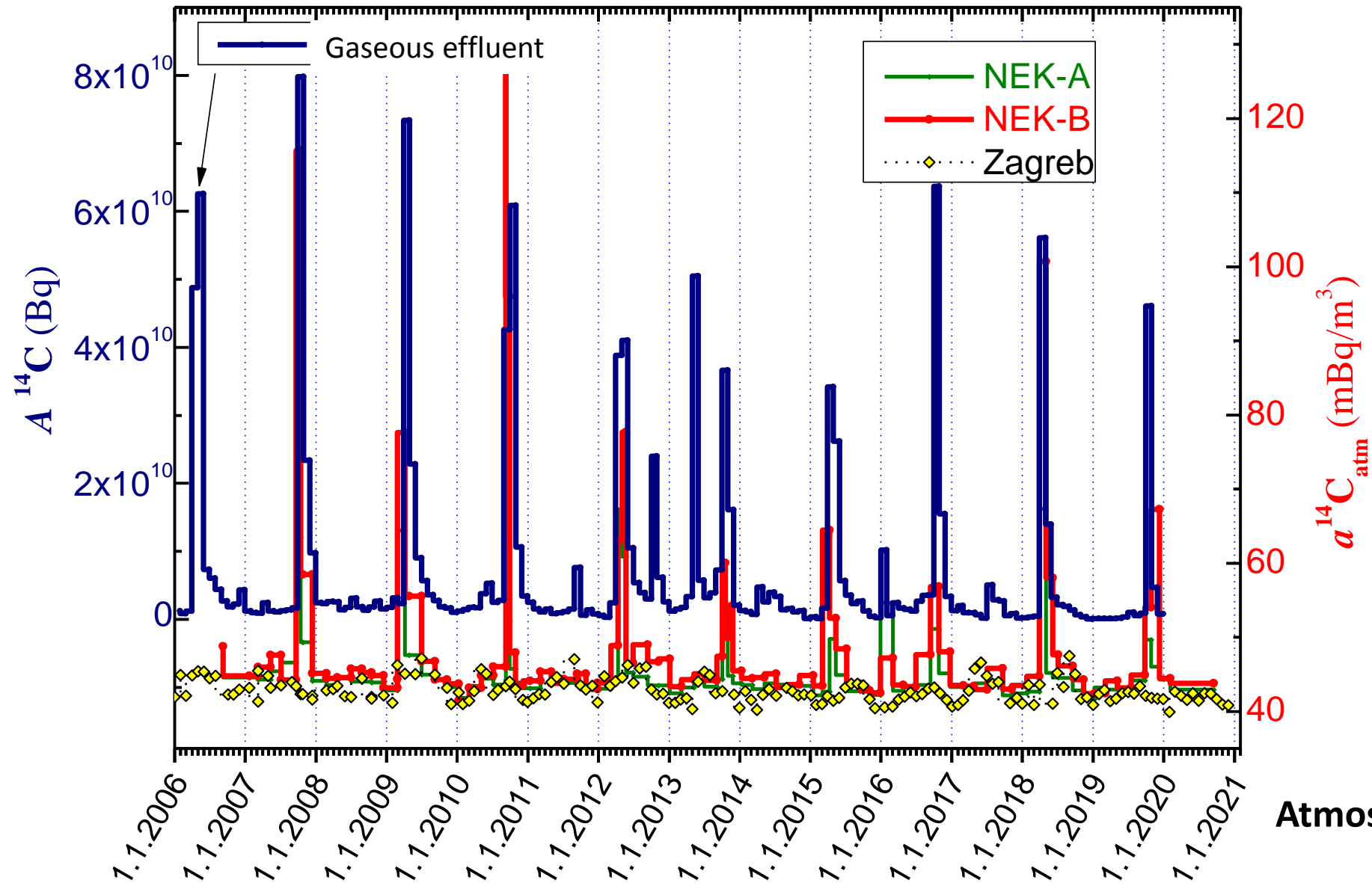
Control charts

Average measured $a^{14}C$ for ANU Sucrose (150.7 ± 1.8 pMC) in good agreement with the true $a^{14}C$ (150.6 pMC).

Average $a^{14}C$ for shell sample is 102.7 ± 1.3 pMC, median 102.7 pMC, range 100.2 – 105.3 pMC.

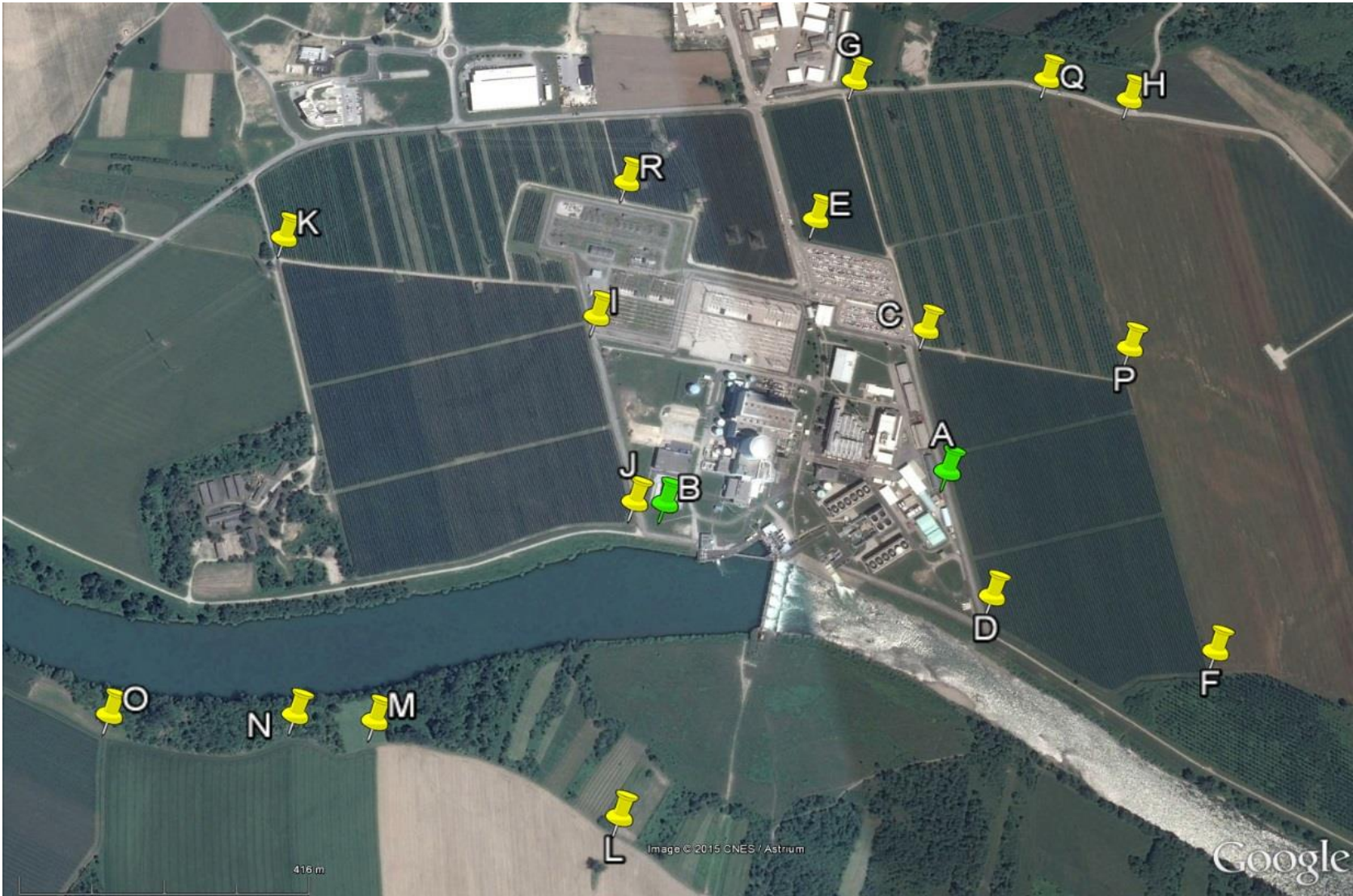


Application of LSC-B - Monitoring ^{14}C around nuclear power plant

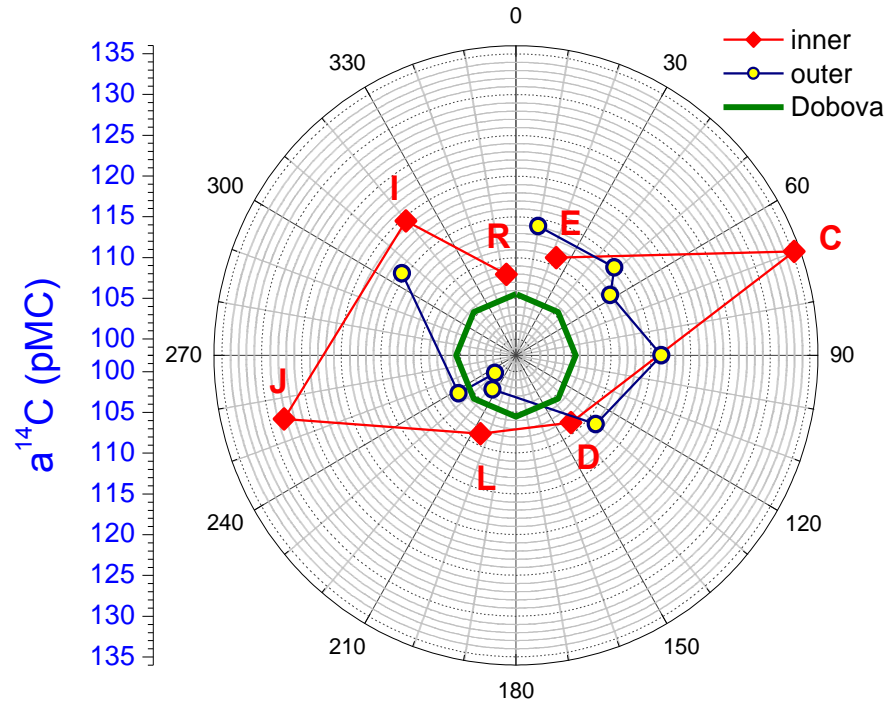


LSC-B

Sampling sites around nuclear power plant

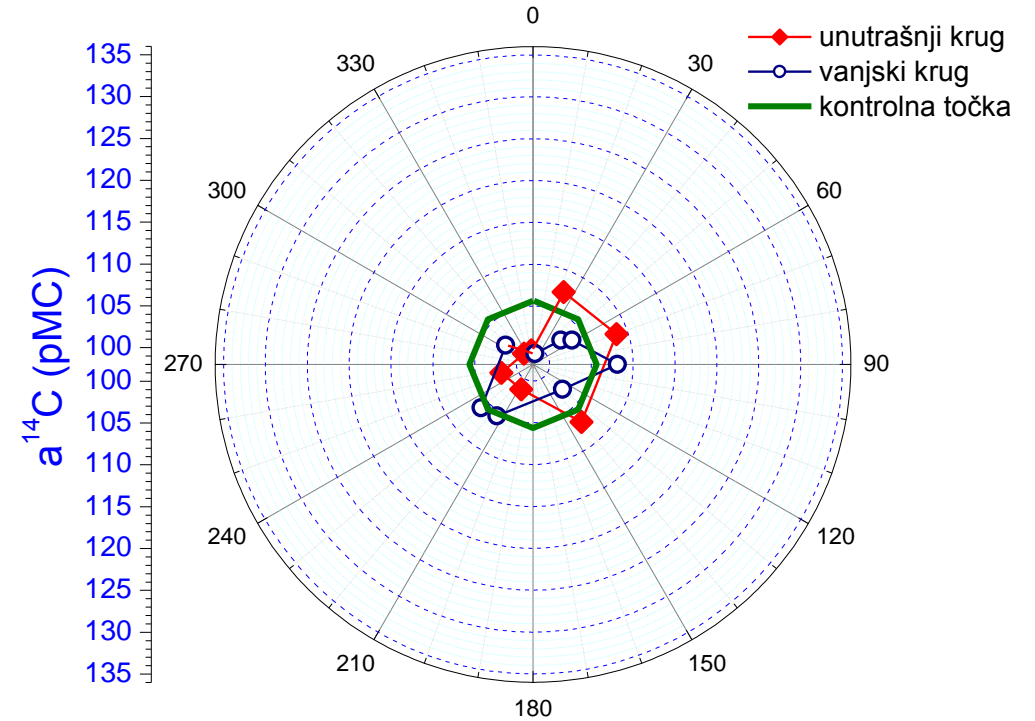


Application of LSC-A - Monitoring ^{14}C around nuclear power plant



6/2009 after spring refueling

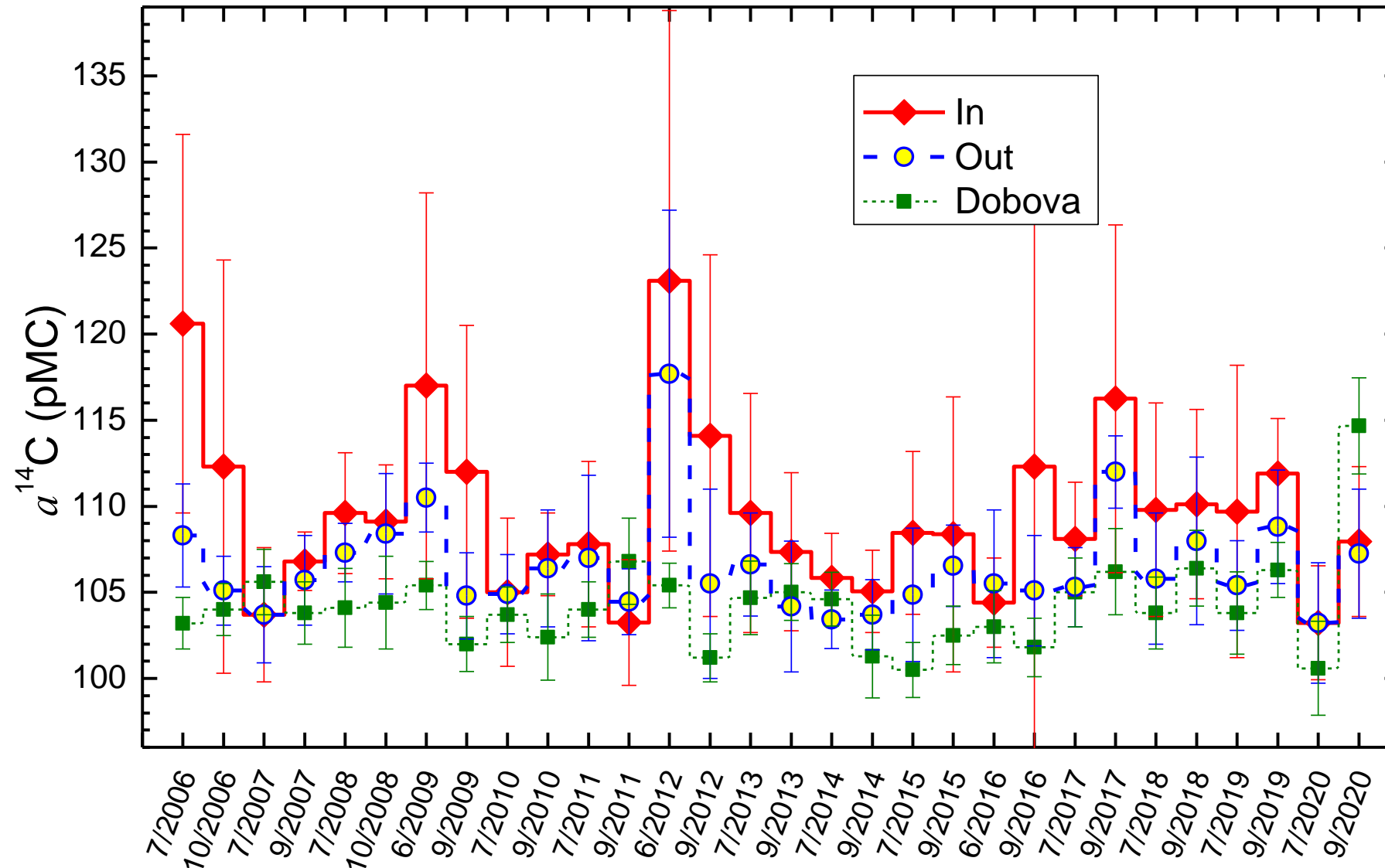
LSC-A



7/2007 – no spring refueling

Spatial distribution of ^{14}C activity in biological samples

Seasonal variations in $\delta^{14}\text{C}$ in biological material around nuclear power plant („In” and „out”) and at the control site, free of npp influence

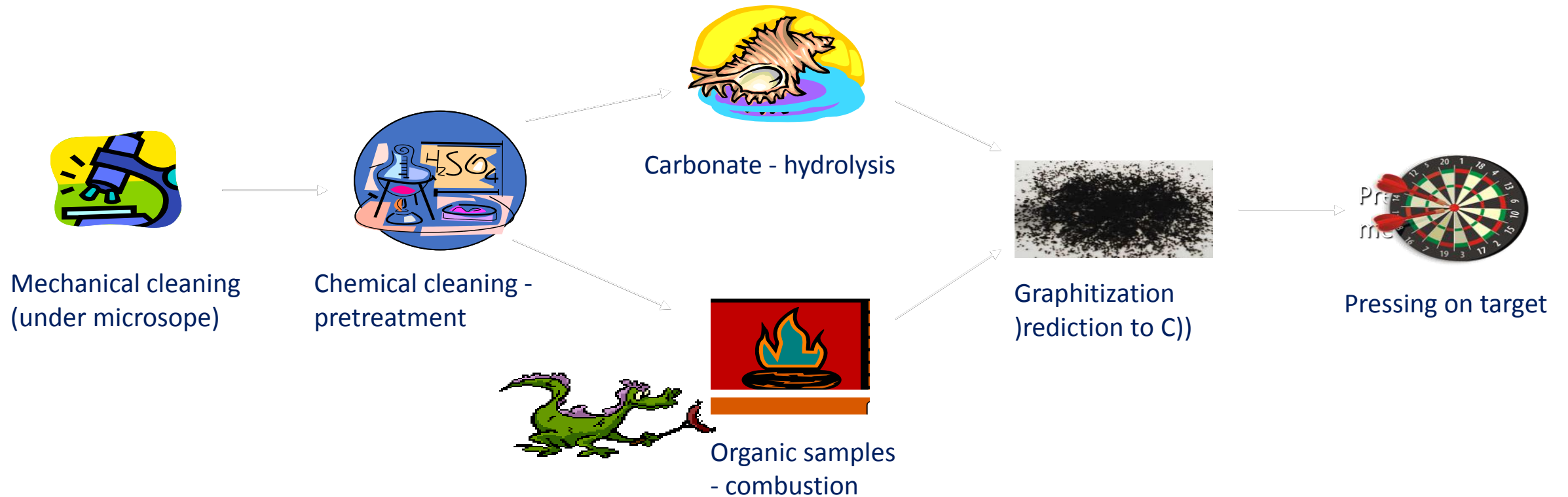


Important notes

- Sample preparation depends on the sample type - the preferred method of sample preparation depends primarily on the nature of the sample and the number of samples that need to be processed (and the required precision)
- Choose the appropriate vial and the proper „Geometry”
- Be consistent in the vial type and geometry
- Quench curves should be prepared for each „geometry”
- Include referent material/standards, background samples

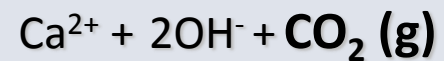
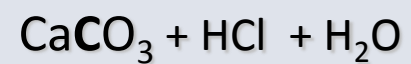
- Similar methods as for radiometric measurement, but arranged for a small samples (mg instead g of samples)
- Very careful with separation of impurities/ cleaning of the original sample (microscope)
- All laboratory accessories (glass and metal) must be thermal processed (heated in oven) to avoid any contamination by recent material during pretreatment

Sample preparation process for AMS-14C



CO₂ production

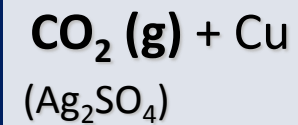
carbonate



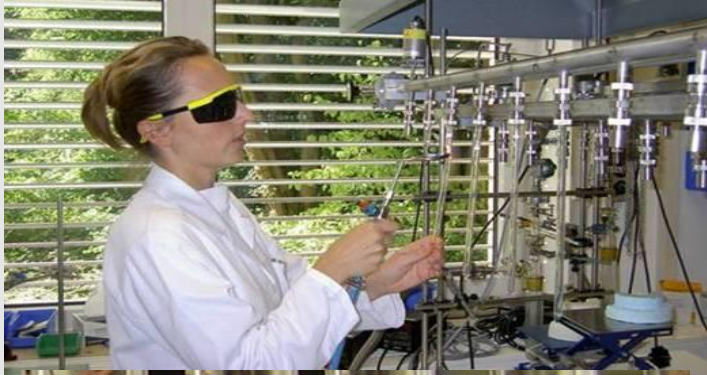
organic sample



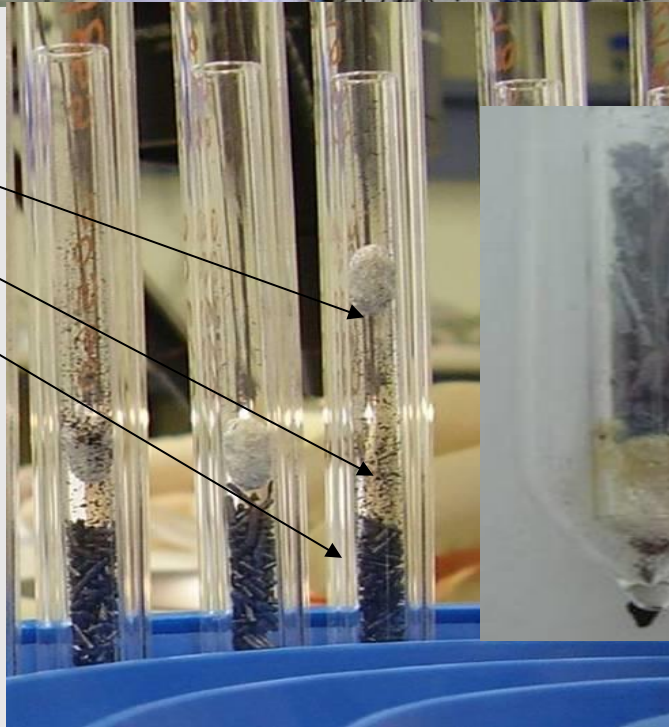
Ag
Δ



Production of CO₂

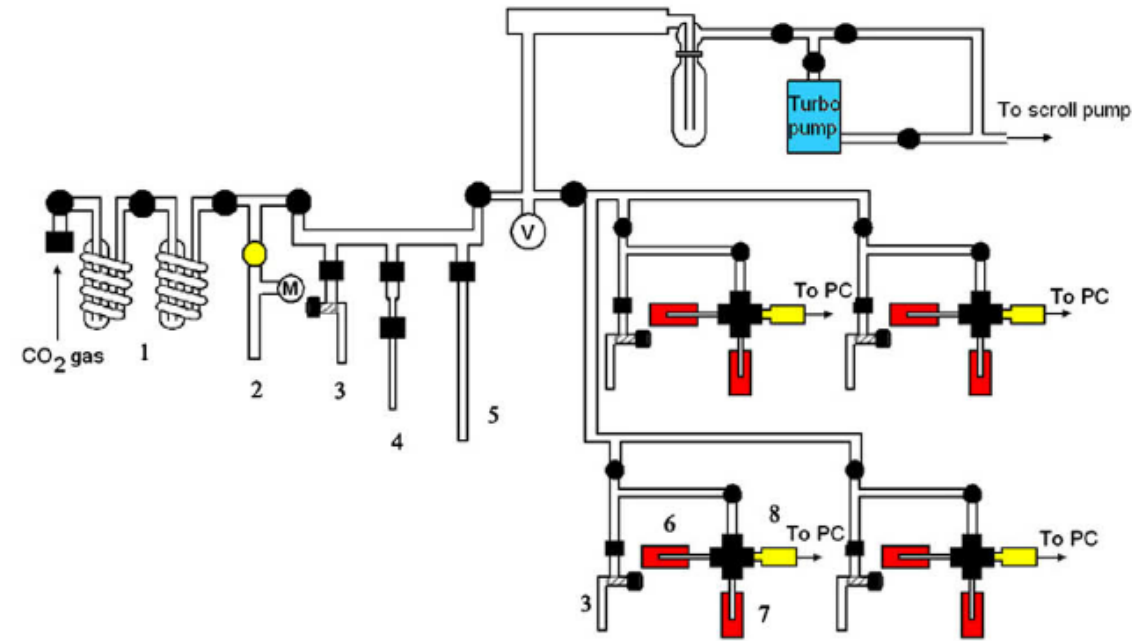
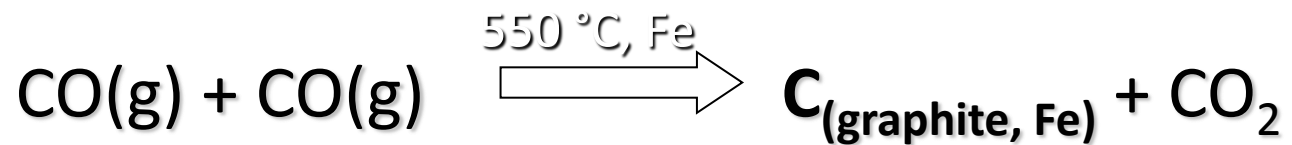
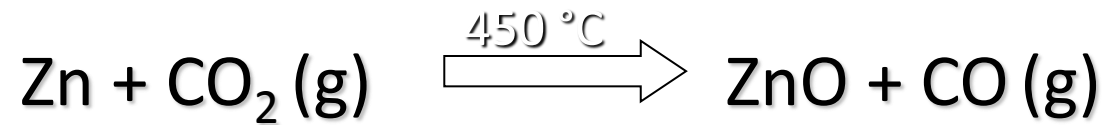


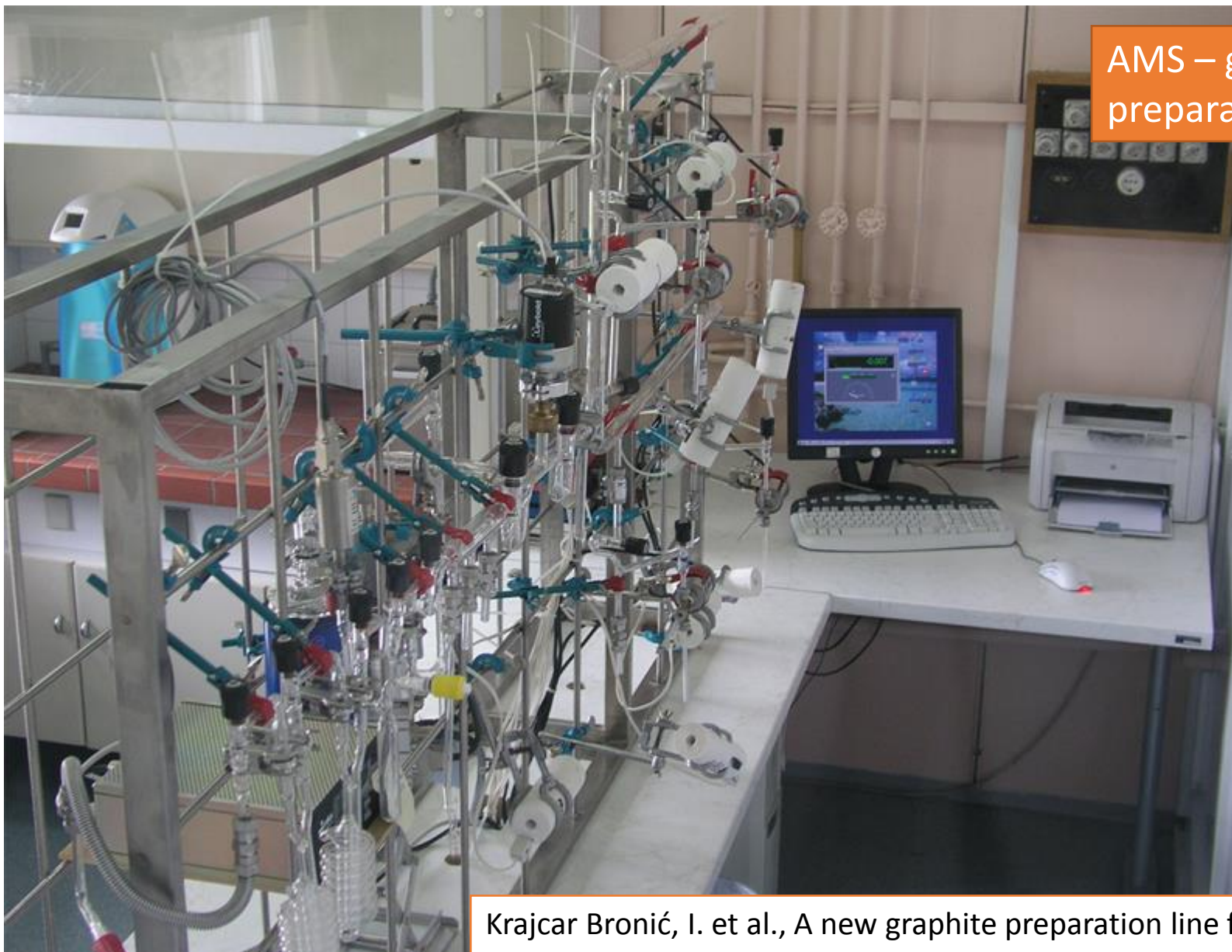
Ag
Sample
CuO



Graphitization

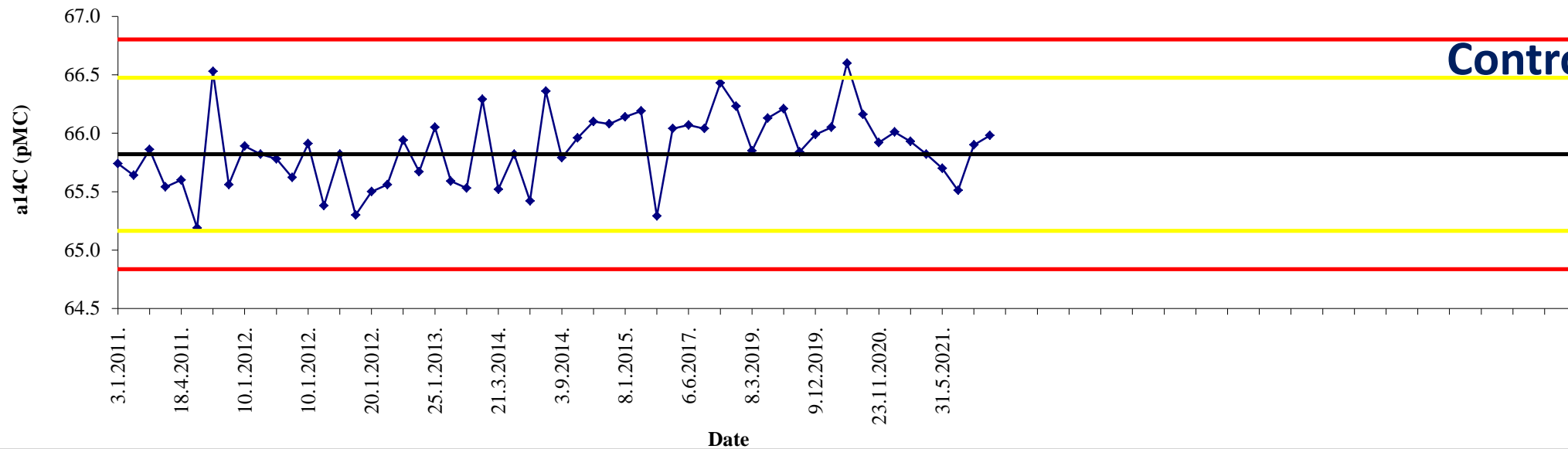
- Reduction with Zn (zinc); or by hydrogen
- Graphite deposited on Fe, also a catalyst



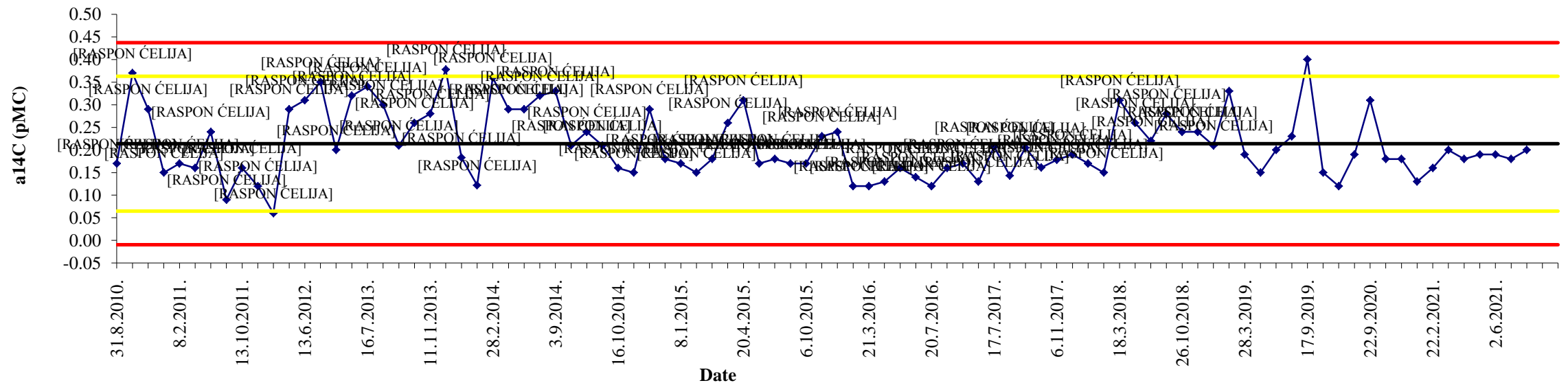


Krajcar Bronić, I. et al., A new graphite preparation line for AMS ^{14}C dating in the Zagreb Radiocarbon Laboratory. *Nucl. Instrum. Methods B* 268 (2010) 943-946
Sironić, A. et al. Status report on the Zagreb radiocarbon laboratory - AMS and LSC results of VIRI intercomparison samples. *Nucl. Instrum. Methods B* 294 (2013) 185-188

Control chart – Humic acid from TIRI – control sample



Control chart – anthracite („background”)



Comparison LSC – AMS, sample amount

	LSC	AMS
Sample type	M (sample) / g	m (sample) / mg
Wood, leaves	20 - 50	10 - 20
charcoal	10 - 15	10 - 20
bones (collagen)	300 - 500	10- 50
shells	50 - 100	30 - 70
water (DIC)	50 – 100 L	1 L
carbonate (sediment)	50 - 100	50 - 100
organic sediment	20 - 50	20 -50
speleothem, tufa	50 - 100	30 - 70
cremated bones (apatit)	50 - 100	1000 do 5000
Mass of prepared sample	4	1.5
Measurement accuracy / pMC	0.5	0.2
Detection limit / year BP	50000	55 000
Time of measurement	20 hours	<30 minutes
No. of prepared samples per week	5	20

AMS vs. LSC

AMS - Small samples (mg, µg)

Advantage

- easier to collect small samples
- Preparation procedure, within 5 days per sample
- graphite synthesis - 4 samples per day (and much more)
- Measurement, 30 minutes per sample
- Non-radiometric → cosmic radiation does not affect the measurement

Disadvantage

- Representativity
- Sensitive to contamination
- Price

LSC - Big samples (grams)

Advantage

- Less prone to contamination
- Representative sample
- Half price of AMS

Disadvantage

- difficult to collect big samples
- Preparation procedure, 7 – 15 days per sample
- C₆H₆ synthesis - 1 sample per day
- Measurement, at least 1 day per sample
- Radiometric → Rn, cosmic radiation!

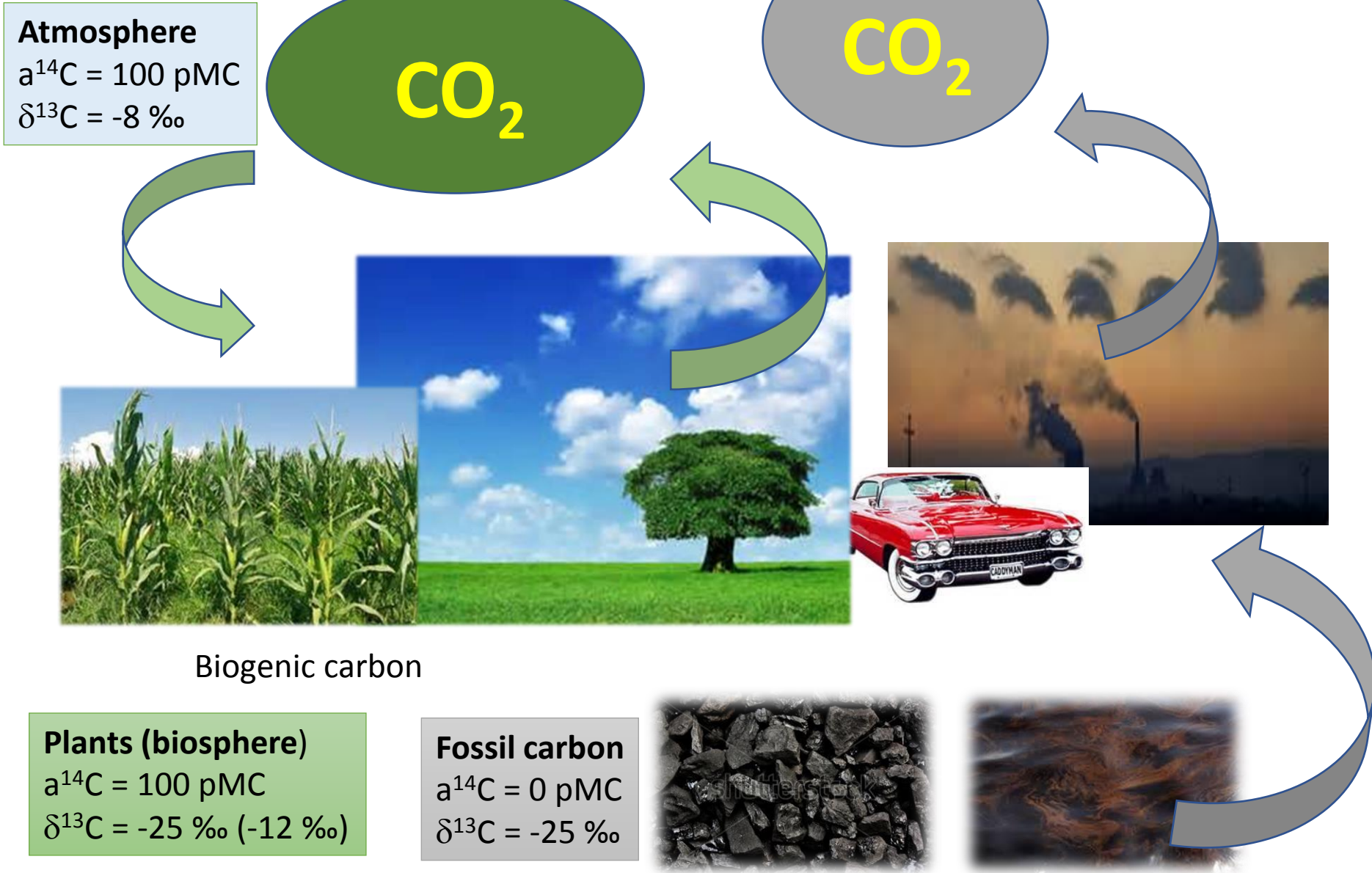
Biogenic component, (bio)fuel

- Liquid scintillation counting of radiocarbon (^{14}C) can also be used to determine the biological content of any organic material.
- All living biological material has a constant amount of radiocarbon per unit weight of total carbon.
- Radiocarbon will disappear from biological material through the radioactive decay.
- Products fully made out of fossil hydrocarbons do not include radiocarbon, as it has decayed completely within the millions of years the product has been underground.
- By determining the radiocarbon activity versus total carbon content, we can determine the biological content of any organic product.

PerkinElmer [Application Note 54](#)

Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis from [ASTM](#) American Society for Testing and Materials, 2012. ASTM D6866-12.

Carbon isotope fingerprint



- Fast, accurate and reliable method of biogenic component determination in various materials (including liquid fuels) is the method based on radiocarbon, ^{14}C
- Various measurement techniques can be used
- The method principle – different ^{14}C activities in two components – biogenic and fossil
- biogenic component reflects atmospheric ^{14}C activity, there is no ^{14}C in fossil component

Fossil matrix of the fuels is either gasoline (benzine, petrol) or diesel (gas oil)

biogenic components/blends - biofuels are usually bioethanol, biodiesel, biogas, biomethanol, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), fatty acid methyl esters (FAMES), hydrogenated vegetable oil (HVO), synthetic biofuels, biohydrogen and pure vegetable oil.

ASTM D6866-12 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. ASTM International. 2012.

How to determine biogenic fraction by the ^{14}C method

Results of measurement are presented as relative specific ^{14}C activity, $a^{14}\text{C}$, expressed in percent of modern carbon (pMC)

100 pMC = 226 Bq/kgC

A material can be composed of a biogenic component (of fraction f_{bio}) and a fossil component (f_f)

$$f_f + f_{bio} = 1$$

The measured ^{14}C activity of such a mixed material, $a^{14}\text{C}_{\text{mix}}$, can be presented as a combination of the biogenic and fossil components:

$$a^{14}\text{C}_{\text{mix}} = f_f a^{14}\text{C}_f + f_{bio} a^{14}\text{C}_{bio}$$

Since in fossil fuels all ^{14}C had been decayed, and $a^{14}\text{C}_f = 0$ pMC, it follows that the fraction of the biogenic component can be determined as

$$f_{bio} = a^{14}\text{C}_{\text{mix}} / a^{14}\text{C}_{bio}$$

Direct measurement of ^{14}C activity in liquid fuels by LSC

Advantage:

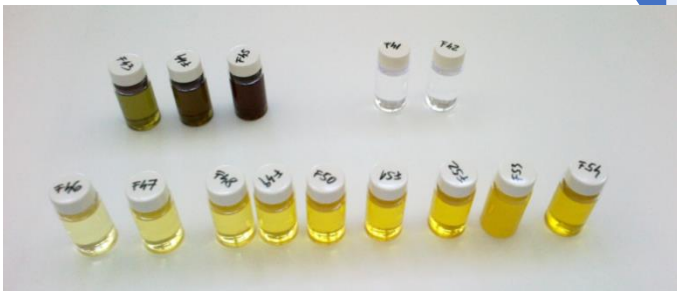
Fast sample preparation
Low cost

Problems:

Not standardized yet
Higher uncertainty

Color quenching

A large variety of mixtures
fossil matrix + biogenic blend



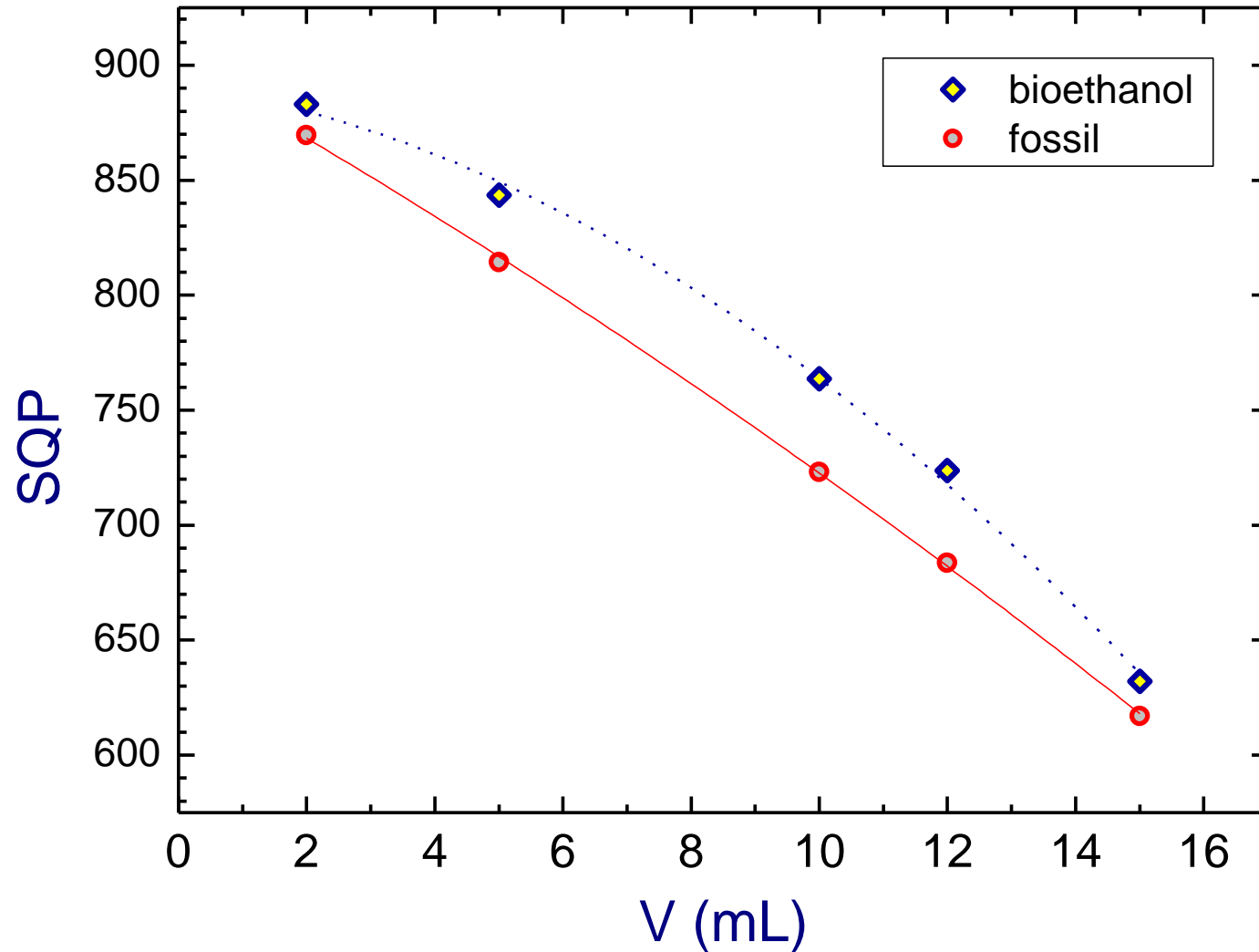


Idea!

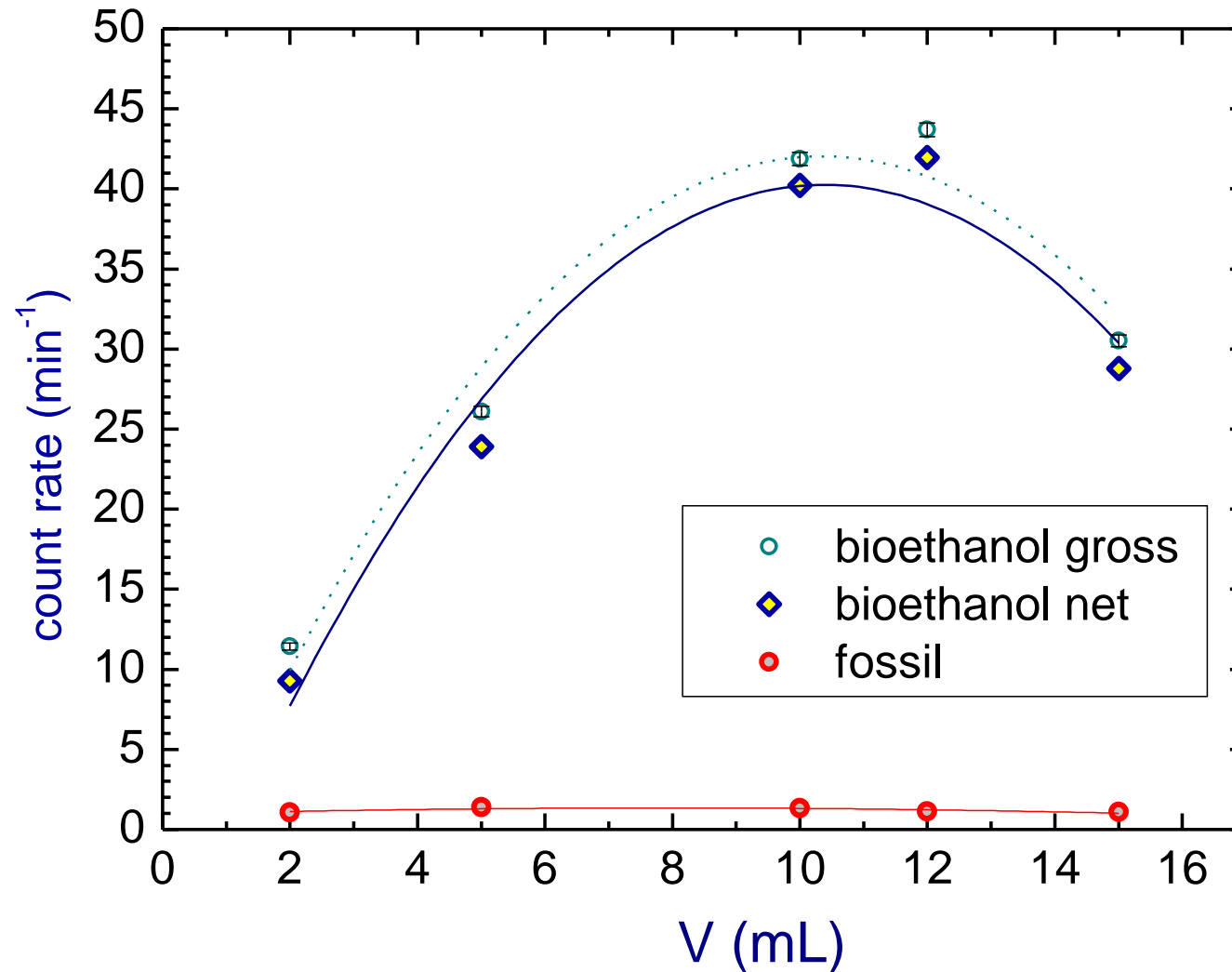
Convert the problem/main drawback to the advantage - **quenching parameter of various samples use as the calibration parameter!**

By using different 100% biogenic and 100% fossil liquids of different colors we determined a relation between the two quantities measured by LSC Quantulus: SQP parameter and count rate

SQP vs volume of fuel in a scintillation mixture, total volume 20 mL,
scintillation cocktail Ultima Gold F (UGF)

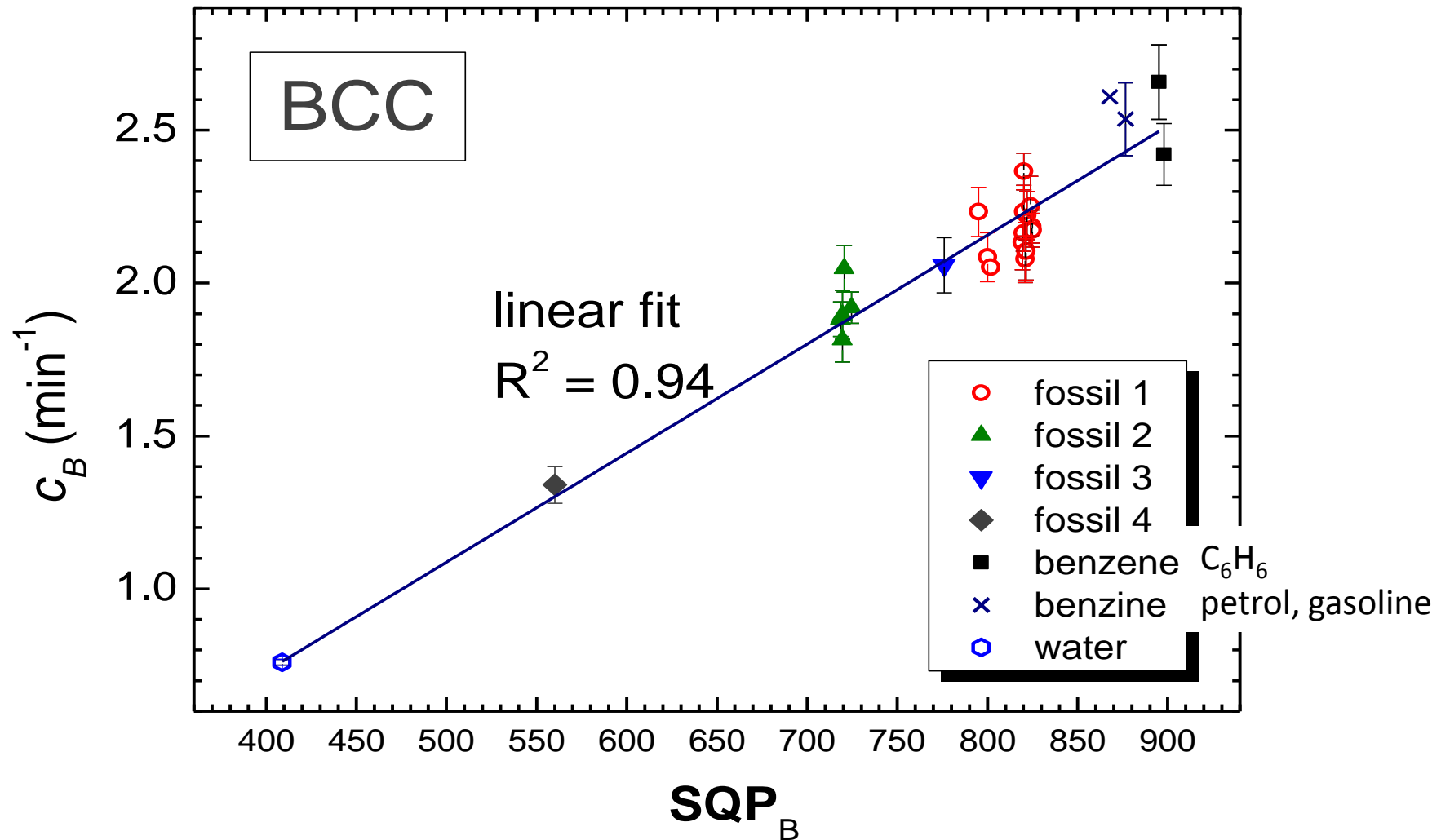


Count rate vs volume of fuel in a scintillation mixture, total volume 20 mL,
scintillation cocktail Ultima Gold F (UGF)

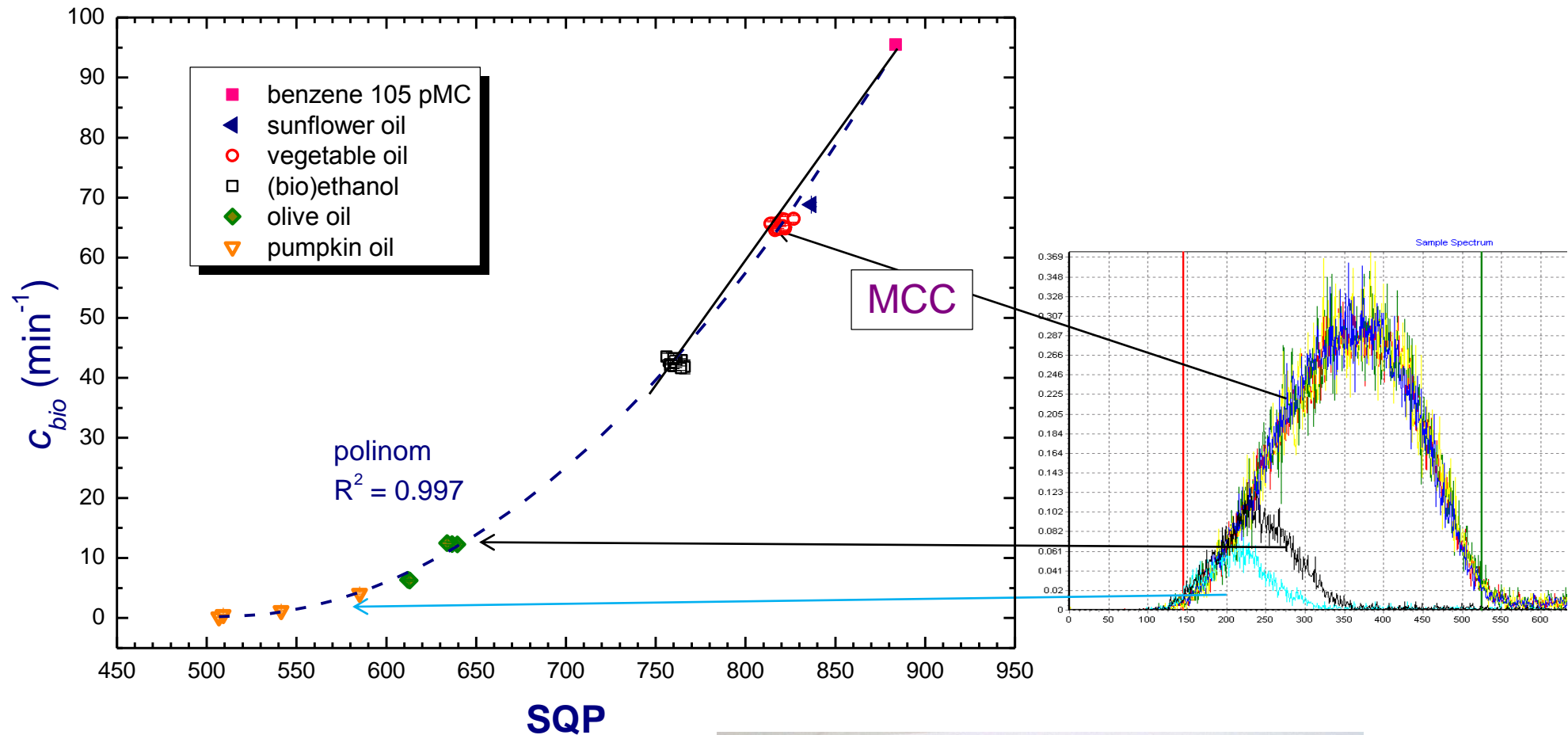


Background calibration curve (BCC)

relates the SQP and count rates of various background samples,
i.e. samples that do not contain ^{14}C

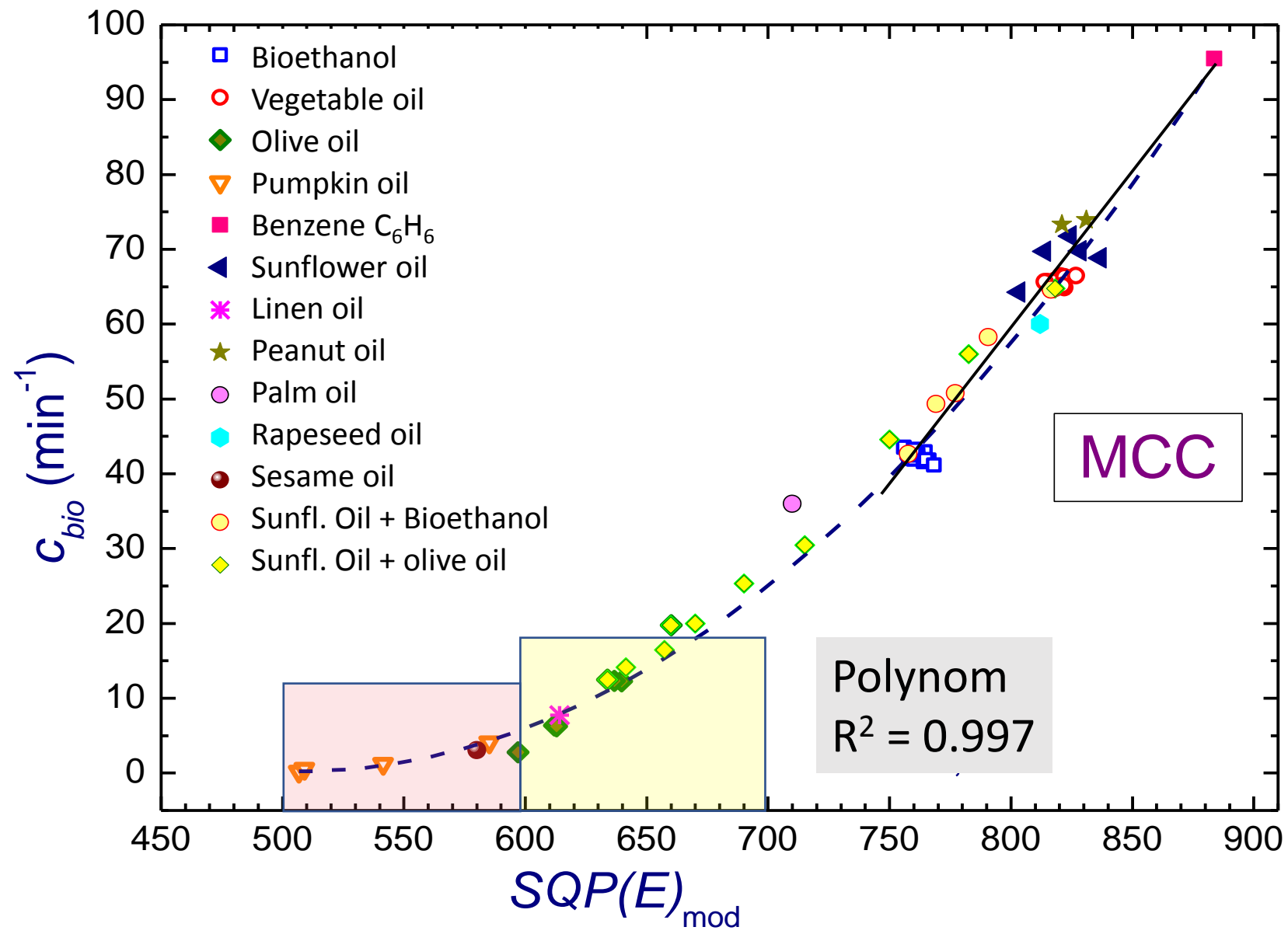


Modern calibration curve (MCC)



Liquid of biogenic origin: various brand of domestic oil, (bio)ethanol p.a., benzene (modern samples)





**Comparison of various biogenic oil samples with the modern calibration curve MCC.
All samples are supposed to be 100%-biogenic.**

LSC-F

The procedure of data evaluation for the unknown sample:

- measurement of SQP and count rate of the sample (SQP, c)
- determination of background count rate corresponding to the measured SQP value by using BCC (b)
- determination of the count rate of the biogenic sample (c_{bio}) corresponding to the measured SQP values by using MCC

The fraction of the biogenic component in the sample is calculated as the ratio of net count rates of the sample to the biogenic material.

All samples should be measured under the same conditions:

- low-potassium glass vials of 20 ml
- scintillation cocktail UltimaGoldF (UGF)
- the ratio sample:UGF 10 ml : 10 ml
- spectra recorded by LSC Quantulus evaluated in the window 124 – 570 channels

$$f_{\text{bio}} = (c - b) / (c_{\text{bio}} - b)$$

The lowest detectable biogenic fraction is 0.5 % for measurement duration of 600 minutes

Intercomparison

- In 2018 international intercomparison study ILC/2018 „Content of biocomponent in liquid fuel samples“ organized by the Institute of Ceramics and Building Materials (Opole, Poland).

10 mL scintillation cocktail UltimaGold F +
10 mL of sample, glass vials

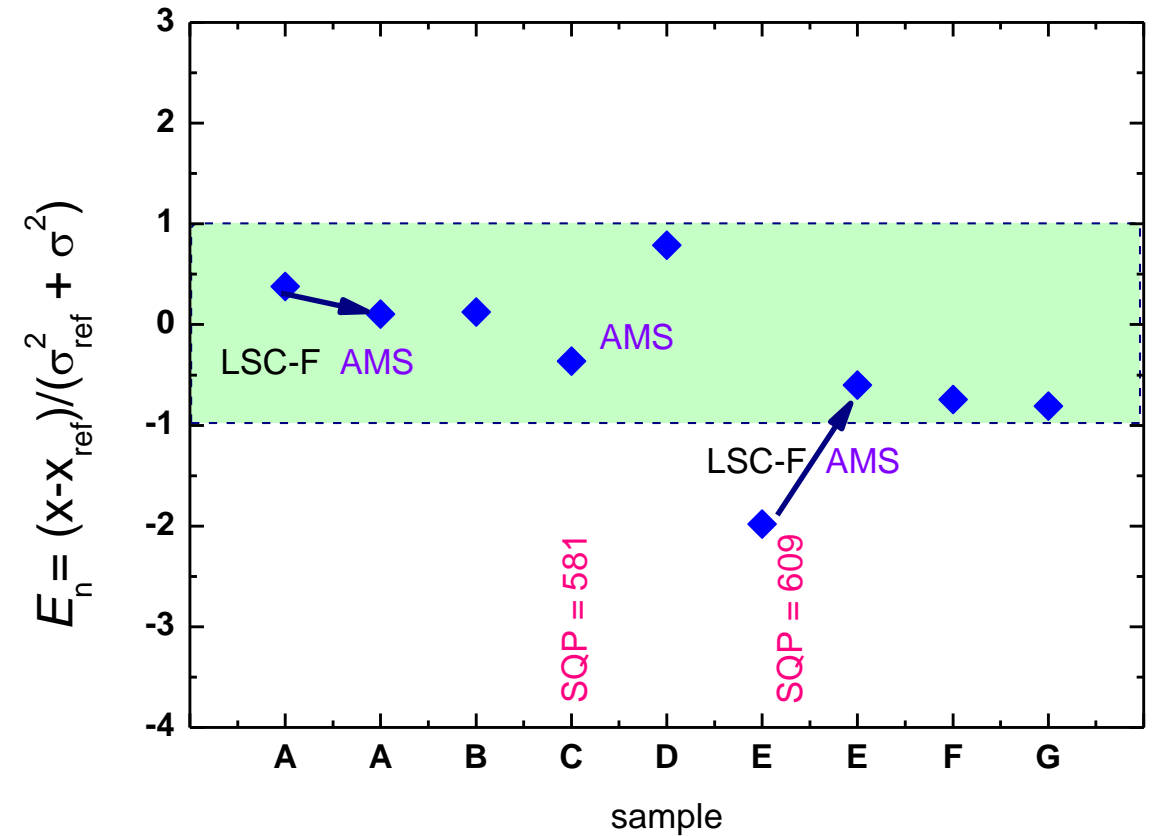
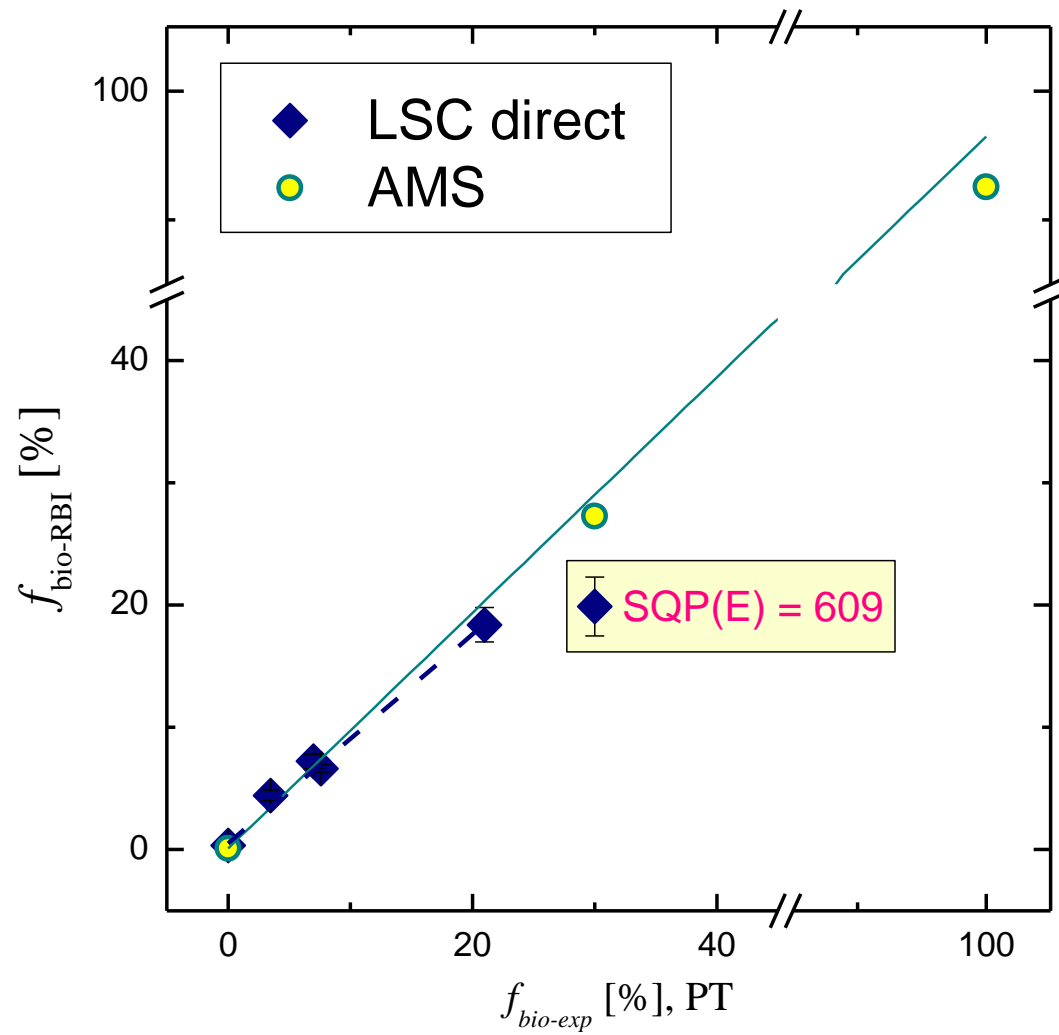


Intercomparison results

Sample code	Sample name	$SQP(E)_{\text{IRB}}$	Expected $f_{\text{bio-exp}}$ [%]	RBI result $f_{\text{bio-IRB}}$ [%]
A	LL/18/0805	804	0.0	0.34 ± 0.25 0.09 ± 0.01^a
B	LL/18/0806	724	7.0	7.23 ± 0.60
C	LL/18/0807	581	100.0	-- 92.58 ± 0.25^a
D	LL/18/1264	758	3.5	4.44 ± 0.43
E	LL/18/1265	609	30.0	19.9 ± 2.4 27.3 ± 0.1^a
F	LL/18/1266	648	21.0	18.4 ± 1.4
G	LL/18/1267	872	7.6	6.64 ± 0.30

a – AMS

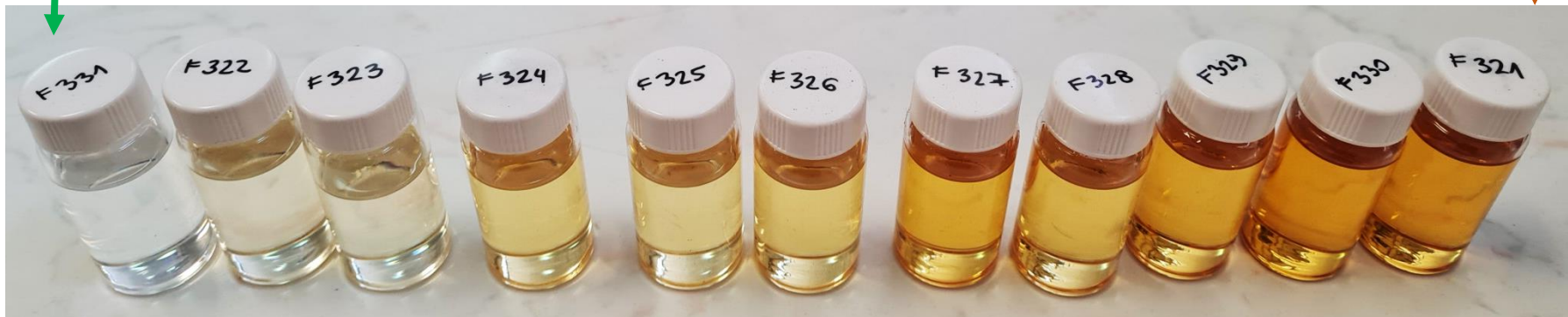
Intercomparison



The obtained results justified previously defined limits of applicability of the direct-LSC method for both quantitative ($\text{SQP(E)} > 700$) and qualitative results ($600 < \text{SQP(E)} < 700$).

Further validation and optimization of the direct LSC method:

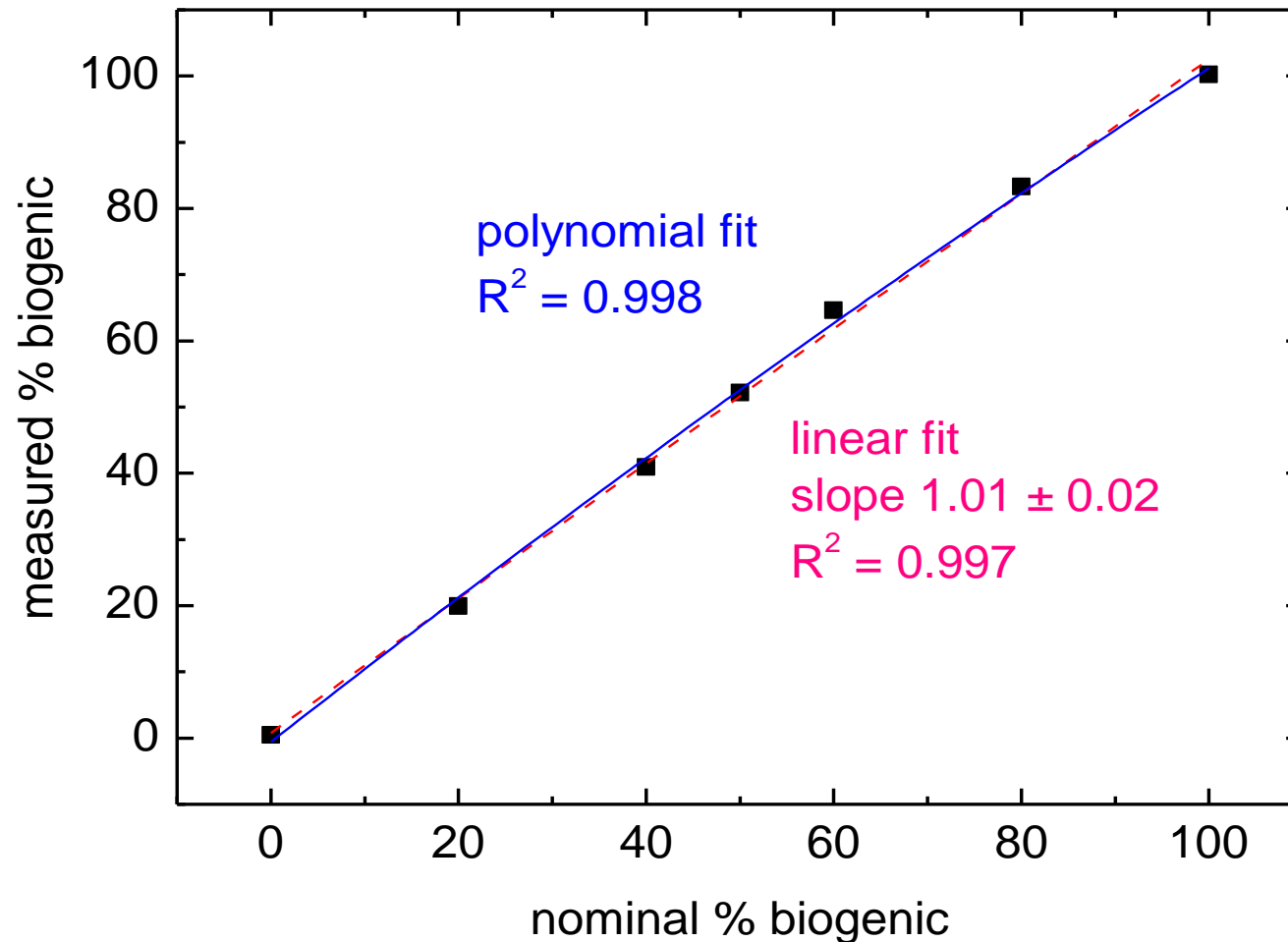
- Z-7226 - **used edible oil (UEO)** was used to test these limits, **SQP(E) = 546**
- AMS: $f_{\text{bio}} = 97.9 \pm 0.3 \%$ (and $\delta^{13}\text{C} = -29.6 \text{ ‰}$).
- We mixed the UEO with the (fossil) petrol (benzine) sample (Z-6266, background sample $f_{\text{bio}} = 0 \%$, good quenching properties **SQP(E) = 864**).
- We monitored changes in the SQP(E), cpm and f_{bio} values in UEO-petrol mixtures in the concentration range 0 – 100 %. The total mixture volume was 10 mL and 10 mL of Ultima Gold F scintillation cocktail was added.



Mixtures of a fossil fuel and bioethanol, total volume 20 mL,
scintillation cocktail Ultima Gold F (UGF)

Mixtures bioethanol + fossil

$V(\text{bioethanol}) + V(\text{fossil}) = 10 \text{ mL}$



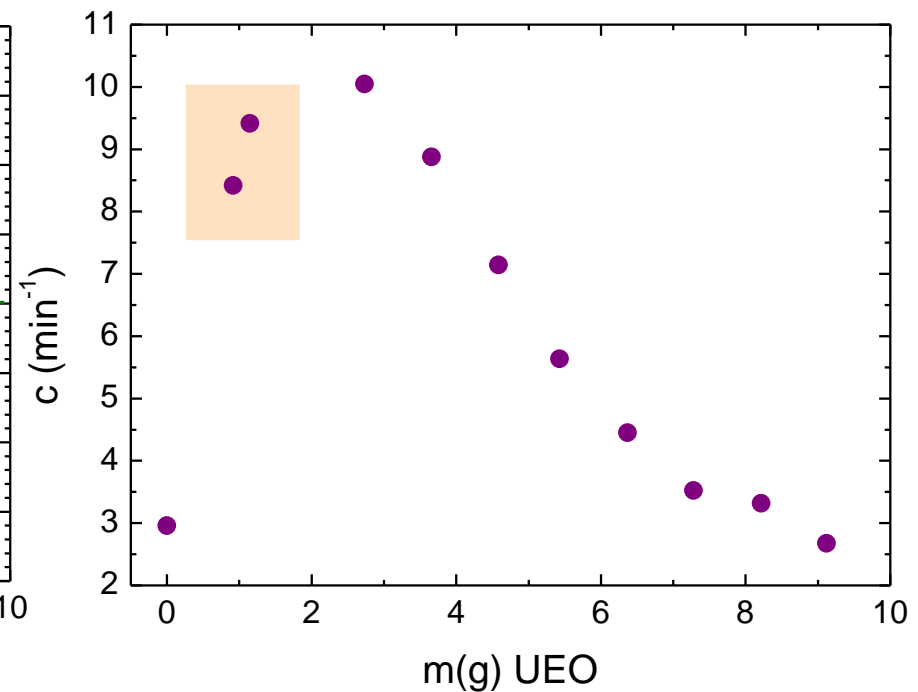
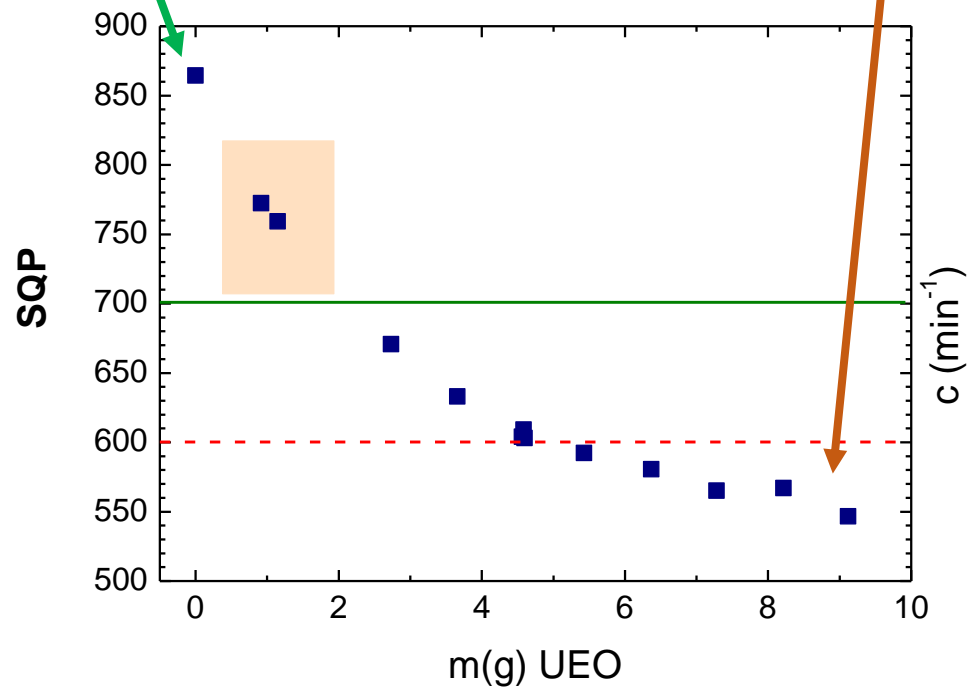
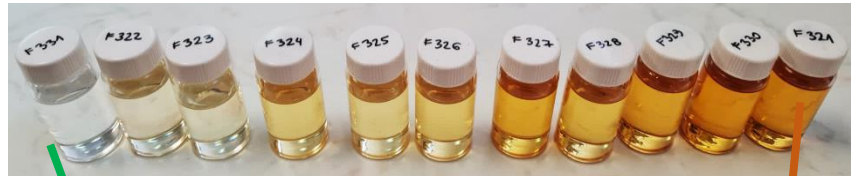
Mixtures of 10 % and 20 % of UEO:

$SQP(E) > 700$

Mixtures containing 30 – 50 % of UEO:

$SQP(E) > 600$

Mixtures containing more than 60 % of UEO: $SQP(E) < 600$



Literature

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