[15] S. J. DAUM & D. R. L. CLARKE, Tetrahedron Letters *1967*, 165; Z. VESELY, J. HOLUBEK & J. TROJANEK, Coll. czechosl. chem. Commun. *33*, 4047 (1968).
[16] H. J. PORTIUS & K. REPKE, Arzneim. Forsch. *14*, 1073 (1964).
[17] G. R. DUNCAN, J. Chromatography *8*, 37 (1962).
[18] Vgl. E. STAHL, «Dünnschichtchromatographie», 2. Aufl., Springer-Verlag, Berlin-Göttingen-Heidelberg 1967.
[19] Vgl. I. E. BUSH & D. A. H. TAYLOR, Biochem. J. *52*, 643 (1952).
[20] G. JUHASZ & CH. TAMM, Helv. *44*, 1063 (1961).
[21] D. H. PETERSON, H. C. MURRAY, S. H. EPSTEIN, L. M. REINEKE, A. WEINTRAUB, P. D. MEISTER & H. M. LEIGH, J. Amer. chem. Soc. *74*, 5933 (1952).
[22] E. WEISS-BERG & CH. TAMM, Helv. *46*, 1166 (1963).

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245. Rapid Instrumental Nuclear Activation Analysis of Rocks, Cements and Meteorites[1]

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Dedicated to Professor W. FEITKNECHT for his 70th anniversary

(1. X. 69)

Summary. The experimental set-up and the method for γ-spectrum analysis as used in the activation analysis of rocks, cements and meteorites by reactor neutrons are discussed. Rapid non-destructive simultaneous determination of several elements is possible. Fractional percent reproducibility is possible for Al, Na and Mn; the determination of Ca, Mg and V in the samples studied is influenced by the Al- and Mn-content, but reproducibility approaches 1% in favorable cases. Accuracy is generally within the limits set by the reproducibility. The minimum weight of the sample is small (10–40 mg), but the grain-size must be below 150 mesh; in the case of meteorites, a grain-size effect has been demonstrated. Representative results for several standard rocks and cements, for 7 L-chondrites, 2 hyperstene achondrites and separate mineral phases of the Elenovka chondrite are given.

1. Introduction. Nuclear activation analysis (NAA) has long been recognized as a most valuable analytical tool. Its main virtues are sensivity and freedom from reagent contamination problems. A typical NAA comprises four steps: irradiation of the sample, chemical isolation of the element sought, measurement of the activity and evaluation of the results. The most time consuming of these steps is usually the chemical isolation of the element sought. Although some attempts have been made to render this isolation automatic [1], it seems more promising to omit it altogether, thus making the whole procedure physical; this way of working is usually termed instrumental nuclear activation analysis (INAA).

In comparision to normal NAA, INAA shows in some instances a reduced sensitivity and necessitates a more sophisticated instrumentation and a more complicated evaluation of the results. On the other hand, INAA has very promising features: it can readily be automated, the evaluation of the results can be computerized and the analysis leaves the sample undestroyed.

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[1] Auf Englisch veröffenrlicht gemäss besonderem Beschluss des Redaktionkomitees.

The elimination of time consuming chemical steps enables INAA to make use of isotopes whose half-lives are too short to allow adequate time for chemical separation. This increases the sensitivity of a number of determinations and also allows determinations which were not previously possible. Working with short lived isotopes (a procedure which we call rapid INAA) is compatible with short irradiations and short measuring times, and this adds another very useful feature to INAA: the possibility to deal with a great number of samples in a short time.

Some of the capabilities of rapid INAA are described in this paper. It is based on work carried out by the activation analysis group of the Eidg. Inst. für Reaktorforschung as part of its program in activation analysis; some of it will be published in a more extended version [2].

2. **Irradiation system.** The irradiation system [3] consists of an irradiation position near the core of the SAPHIR reactor of our Institute and a transport system connecting the irradiation position with the laboratories of the group.

The thermal neutron flux at the irradiation position is $1.8 \cdot 10^{12}$ neutrons/cm^2 s per MW of reactor power; maximum reactor power at the moment is 5 MW, thus giving a flux of $9 \cdot 10^{12}$ neutrons/cm^2 s. The fast neutron flux is approximatly one fifth of the thermal neutron flux.

The samples are packed into polyethylene containers (so-called rabbits) and inserted in the laboratory into the pneumatic transport system. The loaded containers are shot by suction into the irradiation position for a predetermined and accurately reproducible time; thereafter they return automatically to the loading station. Time for transport over a distance of 120 m is 7 s.

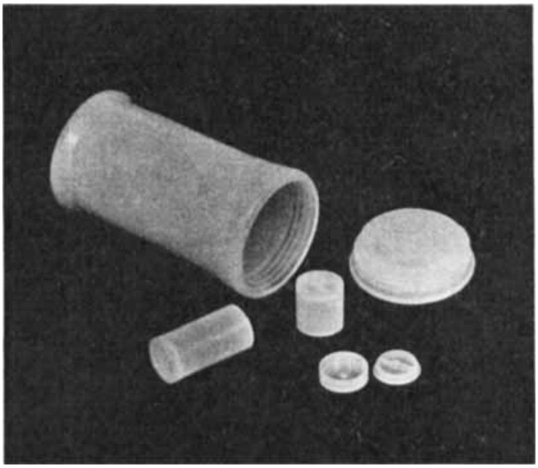

Fig. 1. *The 'rabbit' used in the pneumatic system*
The smaller capsules shown (3 sizes) are used as containers for the samples.

In view of the great final speed attained by the rabbits and the elevated temperature in the irradiation position, the construction of the rabbits posed some mechanical problems; a container with reinforced rims and a screwed cover proved to be the best (see Fig. 1). In order to minimize the induced activity the rabbits are manufactured from specially pure polyethylene; their usable volume is 12 cm^3.

When the rabbit is in the irradiation position, there is no flux gradient along two of its axes, whereas there is a gradient of 2.5% per mm along the third axis (*i.e.* the long axis). This allows simultaneous activation of 3 samples to exactly the same neutron dose; only when more than 3 samples are activated is it necessary to apply a correction for the flux gradient.

3. Counting and evaluation of the results. The activated samples are usually γ-counted on a $3'' \times 3''$ NaI-crystal coupled to a 256-channel analyzer. The special feature of the system is a chopper-type stabilizer [4] that can deal very efficiently with gain-shifts, including short-term shifts induced by rapidly decaying radioisotopes [5]. All significant time intervals, *e.g.* the time between the end of the irradiation and the beginning of the measurement and the duration of the counting both in real and in life time are electronically measured and printed out. Measuring cycles can be programmed.

The recorded γ-spectra are transfered to a computer and analysed for the contribution of the individual radioactive nuclides present in the sample by a weighted linear least-square fitting procedure [6]. The necessary standard spectra of the pure nuclides were determined once for all with great care and stored in the library of the program. The time taken by the IBM 360 computer for the analysis of a spectrum is of a few seconds.

Obviously the success of this computerised analysis of γ-spectra depends critically on the ability of the gain-stabilizer to correct for both long- and short-term gain drifts, since the method presupposes that the spectra of each individual nuclide in the library and in the composite sample have exactly the same line width and line position. With the chopper-type stabilizer, we were able to use our library for over two years without any need for adjustments; the only limitation was that the total counting rate did not exceed $3 \cdot 10^5$ cpm.

The correctness of the result of the spectrum analysis is judged (a) by the matching of the computed and the recorded spectrum, and (b) by the correct decay of the individual components in a succession of spectra of the same sample.

In general no difficulties were encountered as long as the number and identity of the different activities present in the sample were correctly assessed; however consistent values for aluminium could only be obtained by ascribing 2.24 min to the half-life of ^{28}Al instead of the more usual 2.31 min [7].

The result of the spectrum analysis is given in terms of pulses due to a single nuclide. When dealing with short-lived isotopes (*i.e.* with isotopes whose half-lives are at most a few times longer than the measuring time), care must be taken in converting the number of pulses into activities. The difficulty arises from two facts: (1) these nuclides decay by a considerable amount during measuring; (2) the measuring time proper (TA) is shorter than the elapsed time (TC) by the so-called dead-time, which is composed of a counting rate independent part (TS, due to the stabilizer) and a counting rate dependent part (TM, due to the pulse processing).

The activity of a single component at the beginning of counting (A_0) is given [2] by

$$A_0 = \frac{N}{TM} \cdot \frac{e^{\frac{\lambda \cdot TM}{\eta}} - 1}{1 - e^{-\lambda(TA+TS)}},$$

where $\eta \equiv 1 - TS/TC$ (the duty-cycle of the stabilizer); N is the number of registered pulses due to that activity, and λ is the decay-constant of the nuclide under consideration.

In very special cases, *e.g.* for the nondestructive determination of uranium and thorium, delayed neutrons are counted instead of γ-quanta. This is done in a neutron counter into which the activated samples are directly injected by the transport system [8].

4. Analysis of rocks and cements. In order to evaluate the capabilities of rapid INAA in geology and related fields, a series of standard rocks were analysed. Not all elements lend themselves easily to determination with thermal neutrons. As can be shown by the combination of the nuclear data governing the activation of the nuclides and the emission of γ-rays with the concentration of the nuclides in rocks, the major γ-activities after a short irradiation are due to ^{24}Na, ^{27}Mg, ^{28}Al, ^{49}Ca, ^{51}Ti, ^{52}V and ^{56}Mn; these elements are therefore best suited for determination by INAA in rock samples. Table 1 gives the γ-activities in an activated rock sample produced by the first 25 elements of the periodic table; the elements with atomic numbers 1 to 8, 14, and 15 give only very small γ-activities and are omitted from Table 1.

Table 1. *Some γ-activities of a diabase after a short irradiation* a)

Element	Typical concentration	Active nuclide	Halflife	γ-countrate b)	
				after 1 min	after 20 min
F	250 ppm	^{20}F	11.2 s	0.1	0
Ne	c)	^{23}Ne	38 s	–	–
Na	1.6 %	^{24}Na	15.0 h	16.6	16.4
Mg	4 %	^{27}Mg	9.46 min	19.8	4.5
Al	7.9 %	^{28}Al	2.24 min	4000	12
S	c)	^{37}S	5.1 min	–	–
Cl	200 ppm	^{38}Cl	37.3 min	0.2	0.1
Ar	c)	^{41}Ar	1.8 h	–	–
K	0.6 %	^{42}K	12.4 h	0.1	0.1
Ca	7.8 %	^{49}Ca	8.8 min	5.5	1.2
Sc	34 ppm	^{46}Sc	84 d	0.1	0.1
Ti	0.7 %	^{51}Ti	5.8 min	16.5	1.6
V	260 ppm	^{52}V	3.75 min	60	1.8
Cr	120 ppm	^{51}Cr	27.8 d	0	0
Mn	0.1 %	^{56}Mn	2.57 h	62	57

a) Assumed sample weight 10 mg. Irradiation of 1 min at a thermal flux of $4.3 \cdot 10^{12}$ neutrons/cm^2 s.

b) Activities in units of 10^3 cpm in the most prominent photopeak when the sample is positioned at 1 cm from a 3″ × 3″ NaI(Tl)-crystal. These numbers are taken from [9].

c) Concentration not known, but certainly small.

Furthermore the possibility of determining an element by INAA is given not only by the magnitude of this element's activity, but also by the ratio of this activity to the other activities. Since in rocks the ^{28}Al- and ^{56}Mn-activities tend to dominate, mock-up samples with the following pairs of elements were tested: Mg–Mn, Ca–Mn and V–Al. As expected, the accuracy of the Mg, Ca or V-values deteriorated with decreasing weight-ratios, reaching a value2) of ± 5% for the weight-ratios Mg/Mn = 10, Ca/Mn = 5 and V/Al = $5 \cdot 10^{-3}$. It is hoped that the recent installation of a 40 cm^3

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2) All figures quoted in this paper for errors, reproducibility and accuracy are relative numbers, *i.e.* they are given as percentages of the measured values.

Ge(Li)-detector will ease this situation at least with respect to Ca and V. The accuracy of the Mn and Na values however is not impaired by the presence of the other elements.

Table 2 gives the results of the analysis of 4 standard rocks and one NBS cement sample. The error quoted with the experimental results (first line) is the coefficient of variation of four to six independent replicates. The 'literature value' is given in the second line. As can be seen from Table 2, the reproducibility of the results for Na, Al and Mn is more or less independent of the concentration of these elements, and fractional percent precision is possible. The reproducibility of the results for Mg, Ca and V is influenced by the Mn and Al concentrations as expected, but approaches 1% in favorable cases. Accuracy, as judged from the comparision with the 'literature value' is in most cases within the range of the experimental reproducibility.

Table 2. *Results of rapid INAA of standard rocks and cements*

Material	Basalt BCR-1	Diabase W-1	Dolomitic Limestone NBS 88 A	Portland Cement NBS 1015	Peridotite PCC-1
Mg (%)	1.98	3.72	13.1	2.86	26.6
	(±6%)	(±5%)	(±1.5%)	(±5%)	(±1.7%)
	1.98	3.99	12.9	2.56	26.3
Al (%)	7.12	7.92	0.103	2.57	0.352
	(±0.9%)	(±2.3%)	(±0.9%)	(±2.2%)	(±1.4%)
	7.23	7.86	0.101	2.67	0.355
Ca (%)	5.09	7.63	21.4	43.6	n.d.
	(±7%)	(±2%)	(±2%)	(±1.3%)	
	4.97	7.83	21.55	43.85	
Na (ppm)	23800	16300	120	1150	n.d.
	(±0.9%)	(±1.7%)	(±3.2%)	(±1.1%)	
	24580	15800	ca. 70	1180	
V (ppm)	395	256	2.2	39	30
	(±1%)	(±2%)	(±15%)	(±9%)	(±4%)
	384	256	–	–	31
Mn (ppm)	1465	1345	204	389	893
	(±2.0%)	(±0.9%)	(±1.0%)	(±1.0%)	(±0.6%)
	1350	1327	ca. 230	ca. 410	889

First two lines for each element give the experimental value and the coefficient of variation obtained in this work.

Third line for each element gives the certified value (for the NBS samples); for the other samples it gives the recommended value [10], or, if no value is recommended, the mean of all individual results as cited in [10] [11].

The literature value for Al in PCC-1 is from [12].

For a full appreciation of these results, it must be emphasised that they were obtained on very small samples (not exceeding 40 mg) and in a very short time (irradiation times below 1 min; counting times below 5 min). This combination of rapidity, sensitivity and accuracy is unsurpassed by any other known method.

5. Analysis of meteorites and of separate mineral phases of meteorites. In view of the results obtained on standard rock samples we thought it feasible to apply INAA to stony meteorites and to separate mineral phases of meteorites. This application seemed especially appropriate since (1) considerable doubt as to the validity of earlier analyses has been expressed in the past years and (2) almost always only small amounts of material are available.

One difficulty experienced at first was a coefficient of variation larger than usual. This could be traced to an unhomogeneous distribution of grain sizes of the loosely crushed material in the individual samples. A grain size analysis of the material with subsequent INAA of the fractions gave the data of Fig. 2. The unequal distribution of the elements Na, Mg, Al and Mn is apparent. It is remarkable to note that a strong correlation (with $P \geqq 0.99$) exists between Mg and Mn on one side and between Na and Al on the other side. This is taken as an indication that the abundance ratio of the minerals feldspar (the main source of Al and Na in chondrites) on the one hand, and olivine and pyroxene (the main source for Mg and Mn) on the other hand varies as a function of grain size. We suspect that this effect is one of the reasons for the observation of widely differing results of duplicates (mainly in the analysis of trace constituents in meteorites), which some authors tend to 'explain' by an inherent unhomogenousness of the original sample.

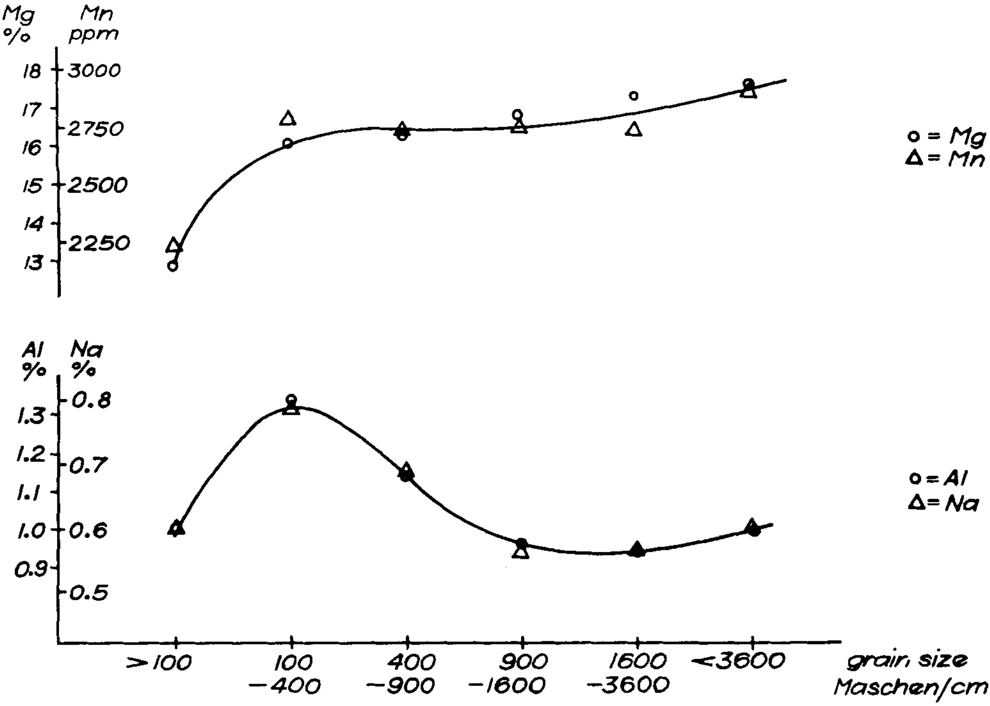

Fig. 2. *The content of Mg, Mn, Al, and Na in different grain size fractions of the Maziba chondrite*

Subsequently all material was powdered to smaller than 150 mesh (= 3500 Maschen/cm²), which brought the reproducibility well within the limits obtained with standard rocks. Table 3 gives the results for 7 L-chondrites and 2 hypersthene achondrites. The precision of the results is indicated by the coefficient of variation of four independent determinations. In comparison to standard wet chemical analysis of

Table 3. *Results of rapid INAA of 7 L-chondrites (a) and 2 hypersthene achondrites (b)*

Meteorite		Mg (%)	Al (%)	Na (%)	Mn (ppm)	V (ppm)
a)	Roy	14.5 (± 2%)	1.09 (± 0.8%)	0.584 (± 1.3%)	2415 (± 0.7%)	67 (± 5%)
	Otis	14.5 (± 2%)	1.10 (± 1.0%)	0.540 (± 1.4%)	2555 (± 0.7%)	71 (± 5%)
	Mocs	15.7 (± 3%)	1.16 (± 1.7%)	0.729 (± 3.0%)	2744 (± 1.0%)	75 (± 5%)
	Bruderheim	15.3 (± 3%)	1.17 (± 1.2%)	0.730 (± 0.7%)	2628 (± 0.3%)	68 (± 5%)
	Elenovka	16.3 (± 3%)	1.17 (± 1.0%)	0.727 (± 1.3%)	2725 (± 0.9%)	75 (± 5%)
	Holbrook	15.9 (± 2%)	1.21 (± 3%)	0.737 (± 1.8%)	2736 (± 2.4%)	73 (± 5%)
	Bjurböle	15.9 (± 3%)	1.35 (± 1.7%)	0.770 (± 0.6%)	2784 (± 0.8%)	78 (± 5%)
b)	Roda	15.4 (± 4%)	0.97 (± 2%)	0.049 (± 2%)	3750 (± 1.0%)	98 (± 5%)
	Ellemeet	15.7 (± 4%)	0.44 (± 3%)	0.043 (± 2%)	4350 (± 1.0%)	200 (± 2%)

stony meteorites (which – it will be remembered – needs more material and more time by orders of magnitude), INAA gives more precise results for Mn, Na and Al, about equal results for V, and inferior results for Mg. Ca-analysis in chondrites is excluded by a very unfavorable Ca/Mn weight-ratio of about 5.

Full use of the sensitivity of INAA had to be made in the analysis of separate mineral phases of the Otis and the Elenovka chondrites, since the process of fractionation is very exacting and the amount of material available for analysis did not exceed 30 mg. In the case of the metal fractions the composition of the total activity is such that further elements become accessible to rapid INAA: copper (*via* 5.1 min ^{66}Cu), cobalt (*via* 10.5 min ^{60m}Co) and nickel (*via* 2.56 h ^{65}Ni). Chromium and gold (*via* ^{51}Cr and ^{198}Au) are determined after a longer decay of the samples. Typical results are given in Table 4; these results have been used to establish the production rates of spallation isotopes for different target elements in meteorites [14].

Table 4. *Results of rapid INAA of separate mineral phases of the Elenovka chondrite*

Mineral fraction	Na ppm	Mg %	Al %	Ca %	V ppm	Cr ppm	Mn ppm	Co ppm	Ni %	Cu ppm	Au ppm
Olivine	1140	21.7	0.18	–	31	1840	3530	–	–	10	–
Pyroxene	6540	16.5	0.99	1.0	61	1860	3250	–	–	10	–
Feldspar	40000	–	6.16	6.4	93	2400	990	–	–	–	–
Troilite	254	–	0.087	–	92	7160	190	–	–	82	–
Metal (A)	502	0.8	0.081	–	< 5	1390	156	8200	7.0	110	1.0
Metal (B)	75	< 0.1	0.011	–	< 5	6190	26	3730	31.3	2100	3.3

The purity of the olivine and feldspar phases is 95%, and that of the pyroxene phase 80% as estimated from X-ray diffraction; the troilite phase and metal (B) contain less than 1% silicates, as estimated from microscopy [13].

The author is indebted to many persons at the EIR for their untiring help, especially to Mrs. DULAKAS, to the staff of the SAPHIR-reactor and of the computer facility. Thanks are due also to Prof. GEISS, Dr. GRÖGLER and Dr. BAERTSCHI for their encouraging interest, and to the Institute of Physics of the University of Berne for the procurement of the meteorite samples.

REFERENCES

[1] F. GIRARDI, G. GUZZI, J. PAULY, & R. PIETRA, in 'Modern Trends in Activation Analysis', Texas A & M University, 1965; F. GIRARDI, in 'Nuclear Activation Techniques in the Life Sciences', IAEA, Vienna, 1967, STI/Pub/155.
[2] A. WYTTENBACH, EIR-Bericht, in press.
[3] A. WYTTENBACH, H. WEITZE, & H. DULAKAS, EIR interner Bericht TM-CH-98 (1968).
[4] A. M. COMUNETTI, Nucl. Instr. Methods *37*, 125 (1965).
[5] A. WYTTENBACH, A. M. COMUNETTI, & H. WEITZE, EIR interner Bericht TM-CH-92 (1967).
[6] E. SCHONFELD, ORNL-3975 (1966).
[7] A. WYTTENBACH, & H. DULAKAS, J. radioanalyt. Chemistry *2*, 287 (1969).
[8] A. SCHUBIGER, A. COMUNETTI, J. MOLLES, & A. WYTTENBACH, EIR interner Bericht TM-CH-103 (1969).
[9] H. R. LUCKENS, GA-5896 (1964).
[10] M. FLEISCHER, Geochim. cosmochim. Acta *33*, 65 (1969).
[11] F. J. FLANAGAN, Geochim. cosmochim. Acta *33*, 81 (1969).
[12] W. LOVELAND, R. A. SCHMITT, & D. E. FISHER, Geochim. cosmochim. Acta *33*, 375 (1969).
[13] P. BOCHSLER, P. EBERHARDT, J. GEISS, & N. GRÖGLER, International Symposium on Meteorite Research, Vienna 1968.

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246. Synthese von *trans*-7-Methyl-2,16-dioxo-eicosen-(14)[1]

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Herrn Professor W. FEITKNECHT zum siebzigsten Geburtstag gewidmet

(1. X. 69)

Summary. The synthesis of *trans*-7-methyl-2,16-dioxoeicosen-(14) dicarbonyl-compounds is described.

Im Rahmen unserer Untersuchungen über die Pharmakologie langkettiger Carbonylverbindungen war für uns das *trans*-7-Methyl-2,16-dioxo-eicosen-(14) (**35**)[2]) von Interesse, über dessen Synthese wir hier berichten[3]).

Wir erhielten dieses ungesättigte, verzweigtkettige C_{21}-Diketon in einer 13stufigen Synthese mit einer Gesamtausbeute von 9,2% (dies entspricht einer Durchschnittsausbeute von 82% pro Stufe), deren Verlauf (s. Formelschema) sich in vier Hauptstufen gliedert.

1) *2-Methyl-2-(5-oxo-hexyl)-1,3-dioxolan* (**29**): α-Acetyl-γ-butyrolacton (**25**) wurde durch kombinierte Ketonspaltung und Halogensubstitution mit HBr in 5-Brompentanon-(2) (**26**) übergeführt[4]). Das Brompentanon wurde mit Glykol zum 2-Methyl-

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[1] Teil der Dissertation Joss [1].

[2] Die Numerierung der Formeln entsprechend der Dissertation Joss [1], auf die öfters verwiesen wird.

[3] Betr. Ausarbeitung einer im Makromasstab durchführbaren Synthese anhand von Modellverbindungen s. [1].

[4] Wir versuchten zuerst, das für die C-Alkylierung ebenfalls geeignete, geschützte 5-Jodpentanon-(2) (**37**) durch FINKELSTEIN-Austausch von Jod gegen Chlor in 5-Chlorpentanon-(2) und durch anschliessende Ketalisierung zu erhalten. Die Gesamtausbeute der beiden Stufen liegt aber so niedrig (3–8%), dass wir von dieser Variante absahen (vgl. Formelschema: Nebenvariante).