

# Environment Protection by Practical Chemistry: A General Chemistry Laboratory Course with a Minimum of Chemical Waste

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**Abstract.** A first year chemistry-laboratory course for 170–210 students has been reorganized to minimize its chemical residues by input reduction and substitution, networking of material flows, separate collection, and recycling at the source. Compared to previous years, the problematic wastes were reduced by a factor of *ca.* 100 and total now less than 15 kg per academic year. The general types of student exercises, teaching aims, time tables, and organization were not affected, and the fraction of student time devoted to recycling is less than 10%. Permanent additional manpower and budget increases are not required. The strategies and proceedings are outlined and illustrated for selected student exercises. Implications for environment protection by practical chemistry are indicated.

## 1. Introduction

Worldwide, chemistry laboratories face a problem of chemical wastes which has recently led to unpleasant newspaper headlines [1]. Most institutions properly collect their potentially dangerous residues and comply with government regulations, but often the accumulated quantities are so large that their handling and disposal become difficult [2]. The common routines are also in attractive: at the University of Zürich, more than 20 t of chemical waste have to be disposed annually. *Via* intransparent channels, they probably end mainly in incineration plants and deposits after export. This meets principal difficulties and sharply rising costs, nowadays. In general, first year laboratory courses teach large numbers of students and produce large amounts of exercise residues. To avoid the latter, student organizations have suggested requirement reductions [3]. As an alternative, the introduction of microscaling has been advocated and advertised [4]. For a general solution of the problem, universities call for additional specially trained personnel, intermediate storage installations, and large-sized regeneration facilities. They also appreciate appropriate additional financial requirements [2].

This article describes a different approach: By a large variety of small changes, the laboratory of general chemistry at the University of Zürich has reduced its problematic residues to minimal amounts of now less than 100 g per student and year. Preliminary accounts have found so much attention [5] that a more detailed description

of the strategies seems in time, though the endeavour is not yet fully completed.

We started from a simple observation: general-chemistry student exercises involve the basic techniques for the separation, purification, and conversion of matter, such as crystallization, extraction, sublimation, precipitation, filtration, centrifugation, distillation as well as elementary analytical and synthetic methods. Indeed, these methods could be applied to regenerate chemicals from residues or to make them environmentally harmless. By doing so, students would not only learn chemistry but also engage themselves actively in environment protection. Further, seemingly useless residues become useful ingredients for experiments instead of waste.

The project was started in 1988, and we are not aware of similarly rigorous previous attempts. However, many of our 'innovations' are not totally original, because they relied on techniques which are becoming common in chemical laboratories nowadays.

## 2. The Laboratory Course in General Chemistry

In its present form, the course was established in 1971 and it is offered by the Department of Chemistry. Parallel to lecture courses, it covers the experimental part of introductory inorganic, organic, and physical chemistry [6]. About 26 exercises deal with laboratory techniques, 34 with inorganic, 29 with organic, and 7 with physical chemistry [7].

Annually, we teach *ca.* 170–210 students starting in biology, biochemistry, geology, geography, mineralogy, and a few other subjects. From October to July the students spend nominally 8 h per each of the 30 teaching weeks in the laboratory. There are *ca.* 100 individual workdesks which are used by two students on alternant days. Groups of *ca.* 20 participants are supervised by one tutor, and they follow a common program [7]. The tutors work 8–10 h a week for the course, and are mainly chemistry Ph.D. students. There are two senior assistants and two half-day technicians in charge of the organization and all technical matters.

If, on the average, every student uses for each experiment only 100 ml of solution with a few grams of reactants, the approximately 80 exercises required lead to *ca.* 1'600 kg of residues per year. In fact, until 1988 *ca.* 2'500 kg of them arose, 1'600 kg of which had to be disposed, following the University regulations [8].

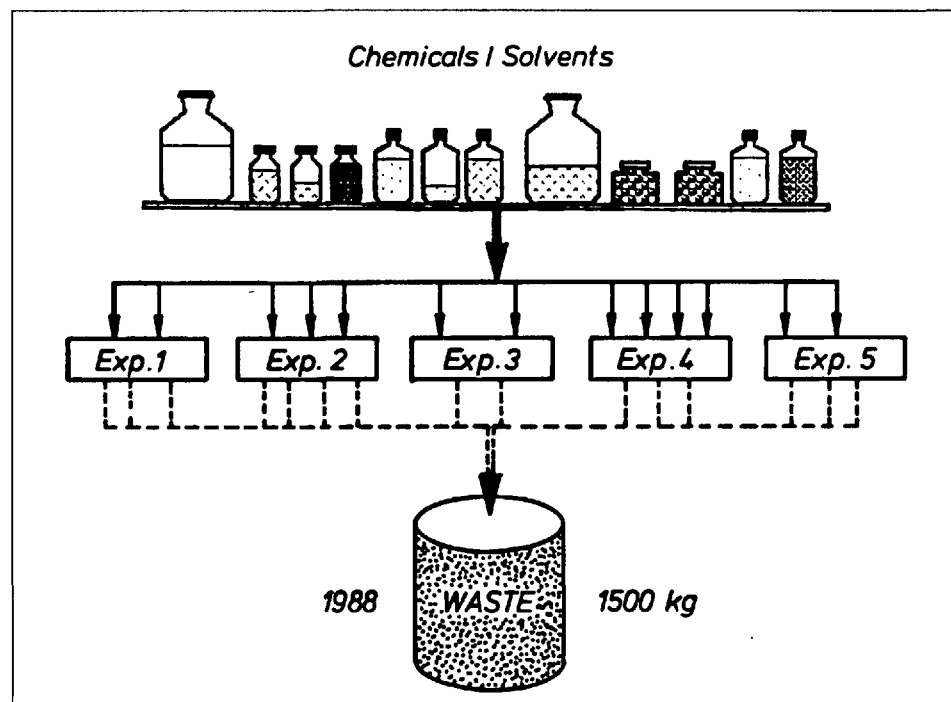


Fig. 1. Normal flow of chemicals in teaching and research laboratories

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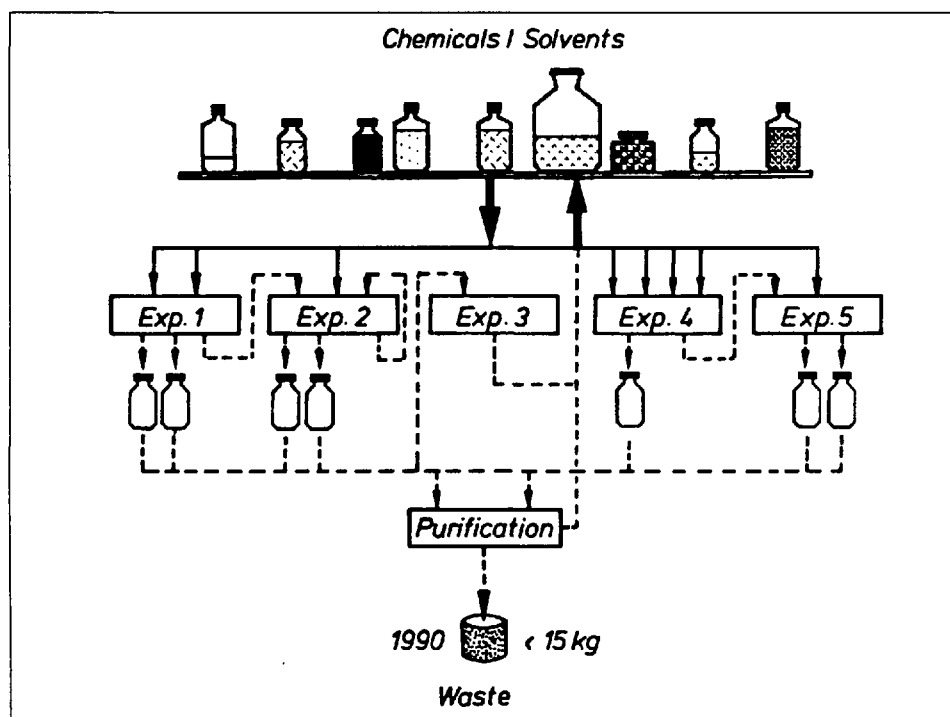


Fig. 2. Flow of chemicals in laboratories with waste minimization

### 3. General Aspects of Waste Reduction and Its Realization

Most chemical teaching and research laboratories work schematically as shown in Fig. 1. According to research or didactic aims, one employs pure chemicals and solvents from a stock. After the individual experiment, the major fraction of the invested matter has become more or less mixed residues. Seemingly of no further interest, it joins the common waste tanks, often separated in non-halogenated and halogenated material only. The mixing in common tanks increases the entropy and decreases the chemical potential of the components, so that workup for reuse is greatly hampered.

Our efforts can be grouped in several categories and are summarized in Fig. 2.

#### Reduction of Quantities

For many exercises, the amount of solvents and chemicals could easily be reduced by factors of 2–10. Microscaling [4] was not applied. However, we had to reduce the size of glassware and to redesign heating baths. Instead of ca. 100 well-thermostatted but big and heavy integrated oil baths, we now use heatable magnetic stirrers with fitting cast-aluminium pots.

#### Substitution

A variety of toxic chemicals like salts of Ar, Sb, Cd, and Hg, the solvents benzene and  $\text{CCl}_4$ , and some analysis reagents were replaced by less problematic ones. For sulfide precipitations now thioacetamide is used, since this solid is much easier to control and handle than the former gaseous  $\text{H}_2\text{S}$ . A couple of dangerous chemicals were retained,

however, since the students should learn to manipulate such material also.

#### Solvent Regeneration

Installation of vacuum controllers and, partly, cooling on rotation evaporators (Büchi AG, Flawil) now allows the regain of up to 90% of nearly all collected organic solvents including  $\text{Et}_2\text{O}$  [9] by the students as integrated parts of exercises. This quick one-step purification was found sufficient to reuse most solvents immediately. Occasional quality checks by GC and precautions against the accumulation of dangerous ingredients ( $\text{Et}_2\text{O}$  is stored over KOH) are provided. This procedure alone brought a considerable waste reduction. The amount of solvents invested shrank by nearly a factor of 4 to now 200 l in the academic year 1989/90. These, we loose mainly by evaporation, and we have taken measures to reduce losses further.

#### Material Networks

As with organic solvents, the use and regain of chemicals has been linked to a network. For instance, in one exercise cyclohexanol is converted to cyclohexene, the starting material for a synthesis of adipic acid. All three compounds are employed in a third exercise and adipic acid even in a fourth. Similar links are being established for wastes. As one can neutralize acid with base residues, one can eliminate oxidizing with reducing residues or use other remnants for mutual precipitation.

#### Separate Collection of Individual Residues

All individual residues of each experiment dealing with potentially dangerous chemicals are collected separately. From experience, we learned that only high

quality fully transparent glass containers are suited for that purpose, if involuntary mixing of remnants shall be avoided. This collection is the key step for simple workup of residues.

#### Exercises on Chemical Regeneration

Student experiments for the regeneration of pure and useful chemicals from residues were designed and tested. As we had expected, they can be performed on the elementary level and do not require sophisticated theory or instrumentation. For these exercises, we needed some larger glassware and a few larger pieces of equipment. Starting now, students may volunteer for them, and no extra time is required.

The various changes were introduced step by step. Delivering nothing to the central disposal station of the University, the academic year 1989/90 left us with ca. 5 l concentrated oily brown-black organic remnant and ca. 20 residues which have not yet been worked up, because their quantities do not exceed 300 ml. Thus, in comparison to previous years more than 99% of waste are avoided, and quite considerable quantities of solvents and chemicals totalling ca. 50 compounds have been recovered in sufficiently pure form for reuse (Table 1).

The variety of small changes did not alter time-tables, organization, or the general contents of the course. Though nearly all of the regular experiments underwent some modifications (Table 2), we were not forced to abandon a single one only for the purpose of waste reduction. In retrospect, we started without defined plans and developed the proper strategies only gradually. We now would recommend the following procedure for similar modifications: at first, all exercises are scrutinized for problematic residues, and those producing some are investigated for substitution or at least reduction. Direct regeneration of solvents is installed simultaneously. After completion of these measures, the schemes for separate collection of residues are set up and introduced. They themselves suggest material networks which are then established, and the design of special regeneration exercises follows as the last step. Further improvements will result from experience.

To illustrate the above aspects the next chapter deals with four specific exercises.

### 4. Modification of Selected Experimental Exercises

#### Separating a Solid Mixture Via Solubility

In the original version of the exercise, each student was provided with a mixture of carbon powder, lead chloride, and copper(II) chloride hydrate. After stirring with  $\text{H}_2\text{O}$  at room temperature, the slush was filtered and the residue washed with additional  $\text{H}_2\text{O}$  until colourless. The ca. 50 ml of combined filtrates were heated (Bunsenburner), until anhydrous copper chloride resulted. The re-

sidue of the first filtration was then boiled with H<sub>2</sub>O, filtrated hot, and washed with more hot H<sub>2</sub>O. On cooling the filtrates, the lead chloride crystallizes and is obtained by a third filtration. The principal aim of the exercise is to learn filtration, to take advantage of solubility differences, to work clean, and to experience the hydration stages of the copper compounds from the colour changes on solvent evaporation.

The modifications started with replacing the coal by the heavier quartz sand and to collect the three solid residues separately. Besides numerous boiling stones the recovered copper chloride contained lead chloride which was found also in large amounts in the filter papers and the sand. This is not astounding, since the difference of solubilities of lead chloride at 100 and 20° is only a factor of *ca.* 3 [10], and a hot filtration is somewhat demanding for beginners. The boiling stones were then avoided by use of the stirrer heat plate, and the lead chloride replaced by adipic acid. This has a much larger solubility difference, crystallizes faster and is less toxic.

#### Preparation and Study of Chromic Acid

Previously, each student dissolved 5.5 g of K<sub>2</sub>CrO<sub>4</sub> in H<sub>2</sub>O, added 35 ml of conc. H<sub>2</sub>SO<sub>4</sub> and obtained after cooling the deep red needles of CrO<sub>3</sub> on a glass filter. With a tiny fraction, its oxidizing, hygroscopic, and depolymerization properties were observed *via* colour changes. Though CrO<sub>3</sub> is hazardous and possibly cancerogenic [11], the exercise was retained but now only 0.55 g of K<sub>2</sub>CrO<sub>4</sub> are used, the practical minimum. The chromium-containing residues are collected. In a regeneration Cr<sup>VI</sup> is first reduced to Cr<sup>III</sup>. This is precipitated as aqueous hydroxide and then dissolved in 20% H<sub>2</sub>SO<sub>4</sub>. Reoxidation to Cr<sup>VI</sup> is accomplished electrochemically on lead electrodes. Finally, the acid and Cr<sup>VI</sup> concentrations of the resulting solution are determined by titration and adjusted to provide a liquid chromic-acid oxidant needed for the preparation of adipic acid [12]. In this way, *ca.* 10 l of chromic-acid residues were recycled so far. Another 15 l were reoxidized to give *ca.* 1.5 kg of solid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, but the procedures [11] proved to be quite tedious.

#### Preparation of Cinnamic Acid by Knoevenagel-Doebner Condensation

Following a standard procedure [13] *ca.* 0.1 mol of malonic acid and benzaldehyde, 18 ml of dry pyridine, and 0.85 g of piperidine were refluxed at 100° for 2 h. The mixture was then poured on ice/conc. HCl from which the product crystallizes. It is purified by recrystallization using a H<sub>2</sub>O/EtOH solution. Probably because of time restrictions, the yields were rather poor, always.

Reduction of the quantities by 50% worked, but the recovery of the solvent bases is nearly hopeless in this case, since pyridine and H<sub>2</sub>O form an azeotrope [10], and there is

Table 1. *Regenerated Chemicals 1989/90*

Organic solvents	>> 10 l	Acetone, Et <sub>2</sub> O, EtOH, CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>
	≥ 5 l	AcOEt, hexane, MeOH,
	0.5 l	Pyridine
Organic chemicals	≥ 1 kg	Adipic acid, cinnamic acid, butyl bromide, cyclohexene, nitrobenzene, dinitrobenzene
	≥ 100 g	azobenzene, benzoic acid, benzamide, benzylanilide, campher, benzhydrol, luminol, methylorange, orange II, sulfanil acid, phenylacetic acid, fumaric acid, maleic acid
Inorganic chemicals	>> 1 kg	Chromic acid, Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O, Hg
	≥ 1 kg	CuSO <sub>4</sub> · 5H <sub>2</sub> O, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , KClO <sub>4</sub> /KMnO <sub>4</sub> , KNO <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub> , KCr(SO <sub>4</sub> ) <sub>2</sub> , ZnSO <sub>4</sub> · 7H <sub>2</sub> O
	≥ 100 g	Ag, Sn, Zn, S, Ca(OH) <sub>2</sub> , CoSO <sub>4</sub> , CuCl <sub>2</sub> · 2H <sub>2</sub> O, KClO <sub>4</sub> , I <sub>2</sub> , NiCl <sub>2</sub> · 6H <sub>2</sub> O, MnO <sub>2</sub> , PbCl <sub>2</sub>

an excess of H<sub>2</sub>O. A solution to the problem was found [14] by simply distilling off the bases after the reflux stage, first at 100° and then above the melting point of the product. Purification was accomplished as before. Somewhat to our surprise, the yields now approach 100%. Also the time required is shorter, because one crystallization is left out. Unfortunately, on working up the distillate, we still found nearly 30% of H<sub>2</sub>O and some EtOH, whereas less than 10% of condensation H<sub>2</sub>O was expected. The origin is very likely the recrystallization solvent so that the procedure has again to be modified, before we regain at least most of the pyridine.

#### Electrochemical Cells

A simple arrangement consisting of two 50-ml beakers, a U-shaped salt-bridge with diaphragm ends, two metal electrodes, and a device to measure the EMF is used to study a concentration chain and to obtain  $RT/nF$  from *Nernst's* equation, to determine a solubility product and to measure a difference of standard reduction potentials. Formerly, Ag/Ag<sup>+</sup>-cells were employed for the concentration chain. To keep the ionic strength constant, the variation of concentration involves successive replacements of 2/3 of the Ag<sup>+</sup> solution in one half-cell by a neutral salt solution, formerly KNO<sub>3</sub>. To the most diluted Ag<sup>+</sup> solution, one added some NaCl and obtained the solubility product of AgCl. Finally, one measured the EMF for an Ag/Ag<sup>+</sup>/Cu<sup>2+</sup>/Cu-combination.

Now, the previous compensating electronics is replaced by a digital millivoltmeter. Its high sensitivity and input impedance allowed to substitute Cu for Ag and, thus, avoid the usual stains from Ag<sup>0</sup> on cloth, floor, and benches. The second electrode is now Zn, and one measures the solubility product of copper oxalate. Finally, Na<sub>2</sub>SO<sub>4</sub> serves as neutral component, since we use the metal sulfates as components anyway. The large amounts of Cu<sup>2+</sup> (*ca.* 60 l) and Zn<sup>2+</sup> (*ca.* 10 l) residues are worked up in student exercises. For Cu<sup>2+</sup>, a hydro-

Table 2. *Statistics of Exercise Modifications 1988–90*

Modification	% of Total <sup>a)</sup>
None or minor	26
Replaced	30
Substitution of chemicals	40
Reduction of chemicals	25
Technical	52
Direct regeneration	18
Special regeneration	40

<sup>a)</sup> Extracted from Student Guides 1987 and 1990.

xide precipitation is carried out which yields the easily filtered basic sulfate CuSO<sub>4</sub> · 3Cu(OH)<sub>2</sub> instead of the gellous hydroxide, since here sulfate is in excess. For Zn<sup>2+</sup>, a carbonate precipitation at pH ≈ 8 is performed. From the precipitates, crystalline copper and zinc sulfates for reuse are easily obtained.

#### 5. Means and Profits

The modifications of exercises required time for development, test, and formulation. We could not find a similar proceeding in the literature and had to search for tricks in now outdated textbooks. For technical modifications and some apparatus, *ca.* sFr. 300'000.– were invested, including a sFr. 25'000.– donation by *Ciba-Geigy*. This fairly large sum is in part due to our ambition to explore the possible limits of waste reduction. A factor of 5–10 would need much lower means. At present, most of the work is complete. There remained no need for additional manpower nor a larger budget.

One question which can justly be asked is, whether the involvement of students in regenerations does not prevent acquirement of other, more useful topics. This is not so, because the same elementary principles can be used throughout. For example, there is no basic difference between the regeneration of a residue by distillation and the purification of a solvent by the same means. In our case, less than 10% of student time are

devoted to recycling mostly within the regular experiments, and thereby, they also deepen their knowledge of such techniques which may help in their further studies and careers.

The exercise modifications and the regenerations were very well received by all students. Some even helped in term-free weeks. This year, so many already expressed interest in regenerations that we do not have enough residues at hand!

We have also observed that waste minimization leads to synergisms: solvent regeneration not only reduced bills but also the storage space and increased the laboratory safety. The vacuum controllers not only reduced solvent losses, but also cut the pumping time up to 90%. The new heating baths are not only more convenient but also need less electrical power. Finally, the *Knoevenagel* condensation now yields less waste, more product and requires less time.

## 6. Environment Protection by Practical Chemistry

Nowadays, public, journalists, and politicians are well aware of the serious chemical-waste problem. In Switzerland, ca. 60 kg of residues of the types encountered in our laboratory accumulate per person and per year, and the average for our chemistry department exceeds 100 kg per chemist. Obviously, many have not yet fully realized that this is becoming more and more dangerous, both for chemistry and the environment. More alarmed representatives of chemical societies today call for more manpower and large installations to cope with the problem [2]. This article has shown that fairly simple chemical techniques can be utilized to reduce it considerably. There are other research groups and laboratories taking the same course, but they are still few. Therefore, we wish to close with some general recommendations derived from experience.

### Waste Reduction

At present, the largest fraction of chemical wastes are organic solvents weakly contaminated by other material. Their reduction is particularly easy. First, there are new chromatographic techniques which need less solvent. Second, they arise on the level of the single experiment only in rather small amounts, i.e. a liter or so, and most laboratories have the facilities for direct recovery of such quantities. The solvents become waste only because residues from many experiments and researchers join the common tanks. At this stage, the individual contributor loses responsibility, and workup becomes a burden. Consequently, small-scale recovery is to be preferred over central installations.

This also reduces storage and safety problems.

### Disposal Regulations

The previously precious solvents and chemicals are readily available today, and their costs provide no incentive for regeneration. Such incentives are also not offered by the current disposal regulations and their waste classifications. The final destinations dictate burning and burial as only means and aims, regardless of risks and costs. Instead of fearing chemistry so much, governments should encourage direct recoveries much more than hitherto and consult more chemical practitioners for available technical standards, not only for the sake of the environment but also for the saving of mankind's resources.

### Environmental Chemistry

Many universities offer courses in environmental sciences including sections from chemistry, mostly toxicological and analytical aspects. These courses are very good for increasing the consciousness of students but help very little to the solution of practical waste problems. In fact, chemistry provides small scale laboratory methods which are applicable generally, but more or less neglects this aspect in teaching. Consequently, this should be stressed in chemical laboratories throughout, starting in schools and introductory chemistry courses at higher education. A few generations of science students trained in this domain are the best investment for environment protection by chemistry.

Chemistry has contributed so much to welfare and living standards, and must continue to do so. This justified aim does no longer excuse the neglect of the residues, however. In our opinion, at the very source each residue can find recovery and reuse, at least its major part. Governments can stimulate, but each chemist should contribute. Such an environment protection by practical chemistry is a challenge for our science.

The modifications of our laboratory leaned heavily on Prof. C.H. Eugster's perfect original design and organization. We appreciate financial support by the *Kanton Zürich* and *Ciba-Geigy* and thank for its rapid availability. Technical help was obtained from A. Kuehne, H. Schwarz, and B. Thueler and the laboratory technicians A. Bader and A. Frei. J. Bader permanently rewrote the 600 pages of student guides. Thanks are also due to the students of 1988–90 for voluntarily testing new exercises, and Prof. H.G.H. Berke, H.-J. Hansen, J.R. Huber, and G. Wagniere for advice and encouragement. It is a particular pleasure to thank the assistants serving as tutors in the course during the past years: M. Amberg, H. Benz, Dr. S. Bienz, Dr. B. Buchmann, I. Dannecker, W. Fiedler, Dr. B. Glänzer, R. Hany, Dr. K. Heberger, H. Kandler, H. Klotz, Dr. R. Kuhn, Dr. S. Mohanty, Dr. F. Reifler, M. Schwager, E. Schwed, Dr. C. Sontag, M. Walbiner, Dr. Wu Lungmin, and R. Wyler, and the more permanent senior assistants Prof. Dr. K. Lendi and R. Müller. Their enthusiasm formed the basis for this work.

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