

PREPARATION OF PURE GLYCINE USED FOR GROWING OF TRIGLYCINE SULPHATE SINGLE CRYSTALS

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It is known^{1,2} that physical properties of single crystals of triglycine sulphate are influenced by conditions of their growth and by the purity of the starting material. By decreasing the density of structural defects in triglycine sulphate single crystals, the mobility of domain walls increases^{3,4}, while the energy necessary for polarisation reversal decreases; also, the value of spontaneous polarization, the Curie temperature, and the maximum permittivity increase.

In the preceding studies¹⁻⁶ purification was achieved by repeated crystallization of triglycine sulphate (or even glycine). However, this method is not satisfactory, as it gives low yields and is rather laborious. Similarly, the method of zone refining can be hardly used, because of the low thermal stability of the substance. Isolation of impurities by extraction or by precipitation is not suitable in view of the chelating effects of glycine and in view of the fact that the excess of the substances employed spoils the solution. The complicated structure of triglycine sulphate and the high acidity of its solutions makes the purification of the final product rather difficult. Preliminary experiments have shown that the purification of the basic substances prior to the synthesis is more convenient. Sulphuric acid of a high purity degree can be purchased (*e.g.*, H₂SO₄ Merck "Suprapur"). Therefore, our experiments were concentrated on the purification of glycine. This communication describes the removal of trace impurities of metals from glycine by means of ion-exchange chromatography.

EXPERIMENTAL

Semiquantitative emission spectroscopy analysis was carried out using a QU-24 instrument. Quantitative content of various metals was determined by atomic absorption spectrophotometry using a Perkin-Elmer 303 spectrophotometer. The results of the semiquantitative spectral analysis showed that the following elements ought to be investigated: Ca, Mg, Fe, Cu, Na. Their content in various eluates was determined quantitatively by atomic absorption photometry⁷. The eluates obtained by ion-exchange chromatography were diluted to a 7.5% solution of glycine, and the content of the above mentioned metals was determined by the method of standard additions⁷. In this way reliable determination can be made of 0.1 p.p.m. Ca (424 nm), 0.3 p.p.m. Fe (248 nm), 0.01 p.p.m. Mg (285 nm), 0.2 p.p.m. Cu (325 nm), 0.02 p.p.m. Na (590 nm) on 1% absorption. Approximate limits of various determinations are: 0.01 p.p.m. Ca, 0.05 p.p.m. Fe, 0.003 p.p.m. Mg, 0.005 p.p.m. Cu, 0.005 p.p.m. Na.

The purity of the starting glycine (Reanal, Budapest, analytical purity) was determined by the above mentioned atomic absorption photometry and by the semiquantitative spectral analysis from the ashes.

As an ion-exchanger the cationic exchange resin Dowex A-1 (Dow Chemicals, Michigan, granulation 50-100 mesh) was used. This resin contains the iminodiacetic group as a function group⁸. The ion-exchanger was first converted to its H⁺ form by passing through it 100 ml of 2N-H₂SO₄ (Merck "Suprapur") and by thorough rinsing with redistilled water (200 ml). For

experiments with the exchanger in its NH_4^+ form, the necessary $2\text{N-NH}_4\text{OH}$ was prepared by isothermal distillation⁹ into redistilled water. The ion-exchanger was placed into a lucite column 550 mm high and of 38 mm internal diameter. The quality of redistilled water was checked by conductometry; its conductance varied between 2 and $3 \cdot 10^{-6} \Omega^{-1} \text{cm}^{-1}$. All manipulation with solutions and chemicals was carried out in polyethylene vessels. Laboratory glassware was used only for short-time operations.

RESULTS AND DISCUSSION

A suitable procedure for removing metal ions from glycine appeared to be that one that may be used for considerably concentrated aqueous solutions. Most of ion-exchangers generally used are not suitable for this purpose in view of the high concentration of glycine and its chelating effects. On the other hand, Dowex A-1 with its chelate function groups (iminodiacetic acid bound to a styrenedivinylbenzene polymer) sorbs a series of metal ions from a medium of concentrated chelating electrolytes. To estimate the separation properties of Dowex A-1, the following procedure was chosen: 100 ml of 15% aqueous solution of glycine was passed through the ion-exchanger column of the above mentioned dimensions at a flow rate of 10 ml/min. The eluate was held in a polyethylene bottle (with the exception of the first fractions); from there an aliquot part was pipetted and used in the determination of the content of the metals by atomic absorption photometry. The same procedure was used when the resin in the NH_4^+ form was used. Isolation of glycine from the eluate was achieved by partial evaporation of the eluate on a water bath and by drying of the crystals thus obtained at 60°C .

The efficiency of these procedures is shown in Table I and Table II. In comparison with the starting substance, the content of the impurities (Table I) decreased in most cases by more than one order of magnitude. The product obtained in this way was of a higher purity grade than the substance obtained by triple crystallization. The only exception represent ions of iron whose content decreased after passing through the ion-exchanger to 40% of the original value. Table I shows also crystallization distribution coefficients calculated from a simplified relation $K = C_k/C_r$, where C_k is the (weight) concentration of impurities in crystals, and C_r is the (weight) concentration of impurities in starting material. These coefficients — applied to the studied system — show the degree of separation of metal impurities during the first crystallization of glycine from the mother solution. By comparing the degree of contamination after the first and after the third crystallization, it is evident that separation of the impurities in the repeated crystalliza-

TABLE I
Content of Impurities (in p.p.m.) in Glycine

Sample	Ca	Mg	Fe	Cu	Na
Not purified	22.00	5.10	9.30	0.90	12.30
Purified by Dowex A-1 (H^+ form)	0.67	0.07	4.00	0.07	0.27
Single crystallization	7.20	0.80	0.93	0.07	3.34
Triple crystallization	1.00	0.40	0.7	0.07	1.47
Crystallization distribution coefficient	0.33	0.15	0.10	—	0.27

TABLE II
Emission Spectral Analysis of Glycine

Sample	Over 1%	1-0.1%			0.1-0.01%					
Not purified	Si	Ca	Mg Al	Fe	Ti Na	Mn Sn	Cu Li	B	Ge Pb	As V
Purified by Dowex A-1 (H ⁺ form)	--		Si	Ca	Al	Fe Mg			V	Cu Mn
Purified by Dowex A-1 (NH ₄ ⁺ form)	--		Si	Ca	Al Fe		Mg		V	Cu Mn Sn

tions does not occur to the extent that would be expected from the value of the crystallization distribution coefficients. As the content of the impurities is very low, evidently a contamination begins to take place that results from manipulations during the repeated crystallizations. When separating the impurities on the resin in the NH₄⁺ form, unwanted ammonium ions are introduced into the solution and these may spoil the final product. Comparison of the efficiencies of the two procedures (Dowex A-1 in the H⁺ and in the NH₄⁺ form) is shown in Table II. The comparison is based on the results of the semiquantitative spectral analysis.

Besides the high efficiency of the suggested separation procedure, one has to consider a substantial increase in the yield of the final product, too. Triple crystallization yields about 10 to 15% of the original amount, while the ion-exchange separation gives a 80 to 90% yield. The only disadvantage of the latter is the imperfect separation of iron.

It was verified in many experiments that ferrous and ferric ions added in the amount of 10 p.p.m. to a 15% solution of very pure glycine (without Fe) were quantitatively trapped by the ion-exchanger. This is in agreement with the fact that distribution coefficients on Dowex A-1 are very high, namely for Fe³⁺. It follows from a comparison of the values of the stability constants of various metal ion complexes with glycine¹⁰ that of the metals followed in this study the most stable complexes are formed by cupric ions which are quantitatively trapped by the chelating resin used, as their distribution coefficient between the ion-exchanger and the solution is very high. A quantitative sorption occurs, if the solution contains iminodiacetic acid, *i.e.* the same chelating substance which is bound to the organic skeleton of the resin. Ions of iron form with glycine less stable complexes than are those of ions of copper. As addition of iron ions to the solution of pure glycine results in their quantitative trapping, the imperfect trapping of iron impurities is not connected with the chelating effects of glycine. A probable explanation of this phenomenon is that the studied solutions contained iron in a poorly reactive form, *e.g.*, as a colloidal hydroxide, as a hydroxocomplex *etc.*

Imperfect trapping of iron on the ion-exchange resin does not hamper the suggested procedure of preparation of the pure substance for growing of triglycine sulphate single crystals, as the preparation of triglycine sulphate needs necessarily at least two other crystallizations and the crystallization distribution coefficient for iron is favourable.

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**BILDUNG VON FLUORIDKOMPLEXEN
MIT ERDALKALIMETALLEN**

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Die anomale, durch die Bildung des CaF^+ -Teilchens in konzentrierter Calciumchloridlösung verursachte Erhöhung der Calciumfluoridlöslichkeit wurde von Traedwell und Köhl¹ beobachtet. Aus der Änderung des Redoxpotentials des Systems $\text{Fe}^{2+}/\text{Fe}^{3+}$ durch die Gegenwart von Fluoriden und Erdalkalimetallionen kann der annähernde Wert der Stabilitätskonstanten des MeF^+ -Komplexes bestimmt werden². Die verwendete Methode ist jedoch nicht genügend empfindlich, um die Bestimmung der Werte der Stabilitätskonstanten schwacher BaF^+ - und CaF^+ -Komplexe zu gestatten. Daher wurde von den Autoren in der Arbeit² lediglich die obere Grenze des Wertes der Stabilitätskonstanten angeführt und in einer weiteren Arbeit³ wurden diese Angaben gegen die den Nullwert aufweisende Ionenstärke extrapoliert. Tanner und Mitarbeiter⁴ bedienen sich zur Bestimmung der angeführten Stabilitätskonstanten (bei Ionenstärke $\mu = 1$) einer Fluoridmembranelektrode. Neuerdings wurden weitere, im Medium mit $\mu = 0,5$ (NaClO_4) und mit $\mu = 1$ (NaNO_3) gewonnene Daten^{5,6} für MgF^+ -, CaF^+ -, SrF^+ - und BaF^+ -Komplexe veröffentlicht. Die bisher ermittelten Werte zusammen mit den entsprechenden Angaben aus der vorliegenden Arbeit sind in Tabelle I zusammengefaßt.

Die Untersuchung von Fluoridkomplexen mit Erdalkalimetallionen ist vom geochemischen, die Theorie der Migration von Fluoriden in hydrothermalen Lösungen vertretenden Gesichtspunkt aus sehr belangreich. Wichtig ist namentlich die Feststellung genauer Bedingungen der Fluoridio-