

# THE UNIVERSALITY OF THE SOLUBILITY PARAMETER

CHARLES M. HANSEN

*PPG Industries, Springdale, Pa. 15144*



*CHARLES M. HANSEN is a research associate in the Advanced Research Group at the PPG Industries, R&D Center in Springdale, Pennsylvania. He holds a B.Ch.E. degree from the University of Louisville and an M.S. degree from the University of Wisconsin. His work on solvent diffusion in polymers and on the solubility parameter led to a doctorate from the Technical University of Denmark in 1967. Continued study of the solubility parameter has led to the present discussion.*

THE purpose of this plenary account is to demonstrate how some of the physical properties of many common materials can be quickly and easily related to each other through a solubility parameter study. It is hoped that this demonstration will stimulate further activity to the appeal by Burrell (1968) for more theoretical interest in a tool which has already found broad and increasing industrial use. The universality of the solubility parameter was pointed out long ago by Hildebrand and Scott (1949, 1962), who established correlations with surface tension and the critical properties. This presentation describes the general applicability of the solubility parameter to a wide variety of materials by means of numerical relationship. The assignment of such numbers has led to the interpretation of many physical phenomena. More refined theoretical approaches are possible (Patterson, 1968), but simplicity and the excellent accuracy of the predictions possible with a solubility parameter study enhance the use of this tool at all levels of scientific and technological endeavor.

Solubility parameter considerations have helped solve numerous specific problems related to polymer coatings. A typical example is improving the solvent to improve solution stability. Low solution viscosity at high solids is enhanced by selectively using solvents which have a low viscosity to improve the solvent as much as the practical situation allows. Improving the solvent has eliminated some polymer incompatibility situations. Solvent choice influences pigment dispersion as well. Since the phenomena of solution, adsorption, and dispersion are vital to so many varied situations, it is thought that the general principles developed can also be applied to other systems. The first step in applying these principles is to characterize the materials in question by a solubility parameter study.

A solubility parameter study involves contact of a material with numerous, well-chosen solvents under conditions relevant to a given problem, and observation of what

miscibility, polymer solubility, polymer compatibility, adsorption on solid surfaces, dispersion phenomena, solubility of inorganic as well as organic materials in organic liquids, and "salting in" phenomena. Examples show similarities in biologically interesting materials having different chemical structures. Physical similarities among these, inorganic pigments, and inorganic salts are also pointed out in an effort to demonstrate how the solubility parameter can be used to relate some physical properties in many different types of materials. The division of the solubility parameter into parts representing dispersion (London), permanent dipole-permanent dipole, and hydrogen bonding energies of cohesion is necessary to make full use of these concepts. Solubility phenomena in electrolytes can also be studied in terms of the cohesive energy density of the materials involved.

happens in a suitable manner. When the energy properties of the material are similar to those of a given solvent, it will dissolve, swell, or adsorb on the material, as the case may be. The solvents are essentially tools chosen on the basis of their solubility parameters to examine a considerable range of interaction energies with relatively few data. The concentrations employed are intended to reflect behavior relevant to a given situation, but for initial screening 10% solutions in test tubes at room temperature have been found satisfactory for most situations encountered by the author (Hansen, 1967a, b, c, 1968; Hansen and Skaarup, 1967). These conditions are used in the present study, except in special cases. Where swelling is measured, as in cross-linked polymer systems, an excess of solvent is necessary. If necessary, very small amounts of a material may be used in such cases with good success on a comparative basis.

Numerous pigment surfaces have also been examined. In studies with pigments, suspension of the solids indicates adsorption of the solvent and a similarity between bulk liquid energy properties and the surface energy properties of the pigment.

Since all the solvents which are similar in some respect to the material studied are also similar to each other, a suitable interpretation of solvent properties combined with a plotting technique will yield regions of interaction for the material and a physical characterization of its energy properties in terms of solvent energy properties. The nature of the material itself does not seem to influence the case, as long as differences in its physical behavior with various organic solvents can be detected.

The purpose of this account is to focus attention on the usefulness of the solubility parameter concept, and not to review the solubility parameter or the various systems for predicting behavior based on the solubility parameter, since Burrell's review is excellent for this purpose (1968). Of the many means of interpreting interaction data with the help of the solubility parameter, the most accurate and theoretically justifiable system has been called the three-dimensional solubility parameter system (Hansen, 1967a, b, c, 1968; Hansen and Skaarup, 1967; Skaarup, 1968). Other systems have been devised, some based on parameters in addition to the solubility parameter itself, and others dividing the cohesion energy into two parts. Burrell (1955, 1957, 1962, 1968) considered the hydrogen-bonding tendencies of solvents as well as their solubility parameters. The result was a system where solvents were divided into three groups: "poorly,"

"moderately," and "strongly" hydrogen-bonded. This was the first major step toward the practical utility of the solubility parameter concept. Refinements on this system have been proposed by Lieberman (1962), who gave arbitrary numbers to describe hydrogen bonding. A similar approach was taken by Dyck and Hoyer (1964). The most recent refinement of this general approach is to consider three solvent numbers: the solubility parameter, a hydrogen-bonding number, and the dipole moment (Crowley *et al.*, 1966, 1967). This improved the accuracy of the predictions, but also complicated interpretation of data because of irregular solubility plots in three dimensions.

Blanks and Prausnitz demonstrated that the division of the cohesion energy for polar solvents into nonpolar and polar parts led to a system with two parameters having good predictive possibilities (Blanks and Prausnitz, 1964). Alcohols were not treated by these authors. Along these same lines Gardon (1966) developed a fractional polarity concept. Each of these systems has achieved some degree of success, since solubility phenomena are certainly related to the parameters used in the various systems.

The basis of the three-dimensional solubility parameter system is the assumption that the energy of evaporation—i.e., the total cohesive energy which holds a liquid together,  $E$ —can be divided into contributions from dispersion (London) forces,  $E_d$ , permanent dipole-permanent dipole forces,  $E_p$ , and hydrogen-bonding forces,  $E_h$ . Thus,

$$E = E_d + E_p + E_h \quad (1.1)$$

Dividing this equation by the molar volume of a solvent,  $V$ , gives

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (1.2)$$

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1.3)$$

where

$$\delta = (E/V)^{1/2} = (\text{cohesive energy density})^{1/2} \quad (1.4)$$

This is the usual equation for the solubility parameter (Hildebrand and Scott, 1949, 1962).

$$\delta_d = (E_d/V)^{1/2} \quad (1.5)$$

The dispersion component of the solubility parameter.

$$\delta_p = (E_p/V)^{1/2} \quad (1.6)$$

$$\delta_h = (E_h/V)^{1/2} \quad (1.7)$$

Permanent dipole-induced dipole forces are generally small compared to the other forces (Good, 1967), with all errors being largely grouped in the  $\delta_h$  component. The units for each of these parameters are (cal./cc.)<sup>1/2</sup>.

We are thus concerned with the magnitude and the nature of the energies holding a unit volume of a solvent (material) together, and not merely the strength of a particular type of bond. A sketch of this system is given in Figure 1.

The original Hildebrand solubility parameter theory was developed on the basis of London forces alone. This approach showed that if the solubility parameters of two nonpolar liquids are approximately equal, a more negative free energy of mixing can be expected than had their solubility parameters been dissimilar. In the new interpretation of the solubility parameter, it has been assumed that if each of the solubility parameter components for one liquid are, respectively, close to corresponding values for another liquid, then by similarity, the process of their mixing should occur readily with a more negative free energy. This assumption seems to be valid, since the three-dimensional system correlates numerous and varied systems very well, but no precise calculations have been attempted, since there is no detailed theory for this interpretation of the solubility parameter.

### Experimental

Numerous solvents and their respective solubility parameters are given in Table I. Table II lists the materials studied. Table III shows how the solvents chosen interact with selected organic materials. Table IV shows the degree of solvent interaction with a number of inorganic materials in a smaller number of solvents than are included in Table III. The number of solvents can be varied according to the particular problem and solubility parameter range of interest; solubility parameter studies need not be time-consuming.

Where solubility is involved, a clear solution is indicated by 1, partial solution by 2, significant swelling with little or no solubility by 3, lesser degrees of interaction by 4 or 5, and zero effect with a blank. These values are subjective and arbitrary and are used for relative comparisons among the solvents only. A 1 to 4 scale has been adopted for the swelling exhibited by the psoriasis scales,

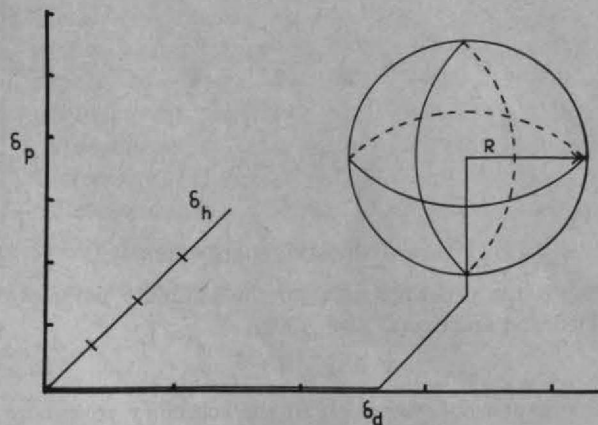


Figure 1. Sketch of a typical volume of interaction

parency. In this special case only a few scales were added to an excess of each solvent.

For the data on the certified ACS grade inorganic salts given in Table IV, 1, 2, 3, or 4 indicates that 5 ml dissolved more than 5.0, 2.0, 1.0, or 0.5 grams of salt, respectively. For pigment suspension data A indicates which solvents suspended a particular pigment for more than a month, and B indicates suspension for shorter periods of time, but significantly longer than viscosity and density comparisons with other solvents would indicate. X indicates additional solvents which frequently suspend other titanium dioxide pigments having different surface treatments. Any suitable scale or method of evaluating the degree of similarity between a solvent and a material is acceptable, since the (present) comparisons are intended to distinguish relative degrees of interaction and not necessarily absolute values. The suspension data for the titanium pigment are included in the middle of Table IV to show how many of the same solvents interact with both the inorganic salts and the pigment surface.

### Evaluation of Results

Since the parameters assigned to the solvents are not precise, their present use in detailed calculations may be questioned. The power of the solubility parameter is its simplicity and generality. Simple, subjective, and relatively unprecise data of the type gathered here allow ready comparisons from which broader relationships may be inferred. These inferences together with the simple data can then provide the basis for more careful and detailed studies if such are desired.

A brief study of miscibility relations, for instance, quickly shows that liquids which have widely different solubility parameters tend to be immiscible. Conversely, polymers having similar solubility parameters tend to be compatible, although numerous other factors affect this phenomenon, including polymer crystallinity, molecular weight, and choice of solvent. These broad and general statements are typical of the type of observation one makes when considering a situation from a solubility parameter point of view.

The data in Table II can be evaluated in terms of the three-dimensional solubility parameter most satisfactorily with a three-dimensional model (see Figure 7 as one example). Two-dimensional plots are useful and generally convey most of the information. Using a computer to plot the data has proved very helpful. Plotting with a unit distance on the  $\delta_z$  axis equal to twice that along the  $\delta_p$  and  $\delta_h$  axes yields essentially spherical interaction regions (Hansen, 1967c). The center of these spheres can be coupled with a radius to characterize a material. The center and radius have been found by trial and error, trying to include the solvents within the sphere while excluding the nonsolvents. In recent work a computer program has been developed to do this more rigorously.

This characterization is empirical and of questionable theoretical value at present, since entropy factors affect the plotted result in an undetermined manner. It is, however, a very useful description which helps compare the solubility properties of numerous solutes in a regular manner. In reality one would prefer to work with free energies, but this is not possible at present although the free energy for the solution process must be near zero on a solubility boundary. Other means of plotting data have

Table I. Solubility Parameters for Solvents

Solvent			$\delta_d$	$\delta_p$	$\delta_h$	Solvent			$\delta_d$	$\delta_p$	$\delta_h$
A01	Methanol		7.42	6.0	10.9	H07	Trichloroethylene		8.78	1.5	2.6
A02	Ethanol		7.73	4.3	9.5	H08	2,2-Dichlorodiethyl ether <sup>a</sup>		9.20	4.4	1.5
A03	1-Propanol		7.75	3.3	8.5	H09	Chlorobenzene		9.28	2.1	1.0
A04	2-Propanol		7.70	3.0	8.0	H10	<i>o</i> -Dichlorobenzene		9.35	3.1	1.6
A05	1-Butanol		7.81	2.8	7.7	H11	Cyclohexyl chloride		8.50	2.7	1.0
A06	Butanol (iso)		7.4	2.8	7.8	H12	Chloropropanol		8.58	2.8	7.2
A07	1-Pentanol		7.81	2.2	6.8	H13	Epichlorohydrin		9.30	5.0	1.8
A08	2-Ethyl butanol		7.70	2.1	6.6	H14	1-Bromonaphthalene		9.94	1.5	2.0
A09	2-Ethylhexanol		7.78	1.6	5.8	K01	Acetone		7.58	5.1	3.4
A10	Methyl isobutyl carbinol		7.47	1.6	6.0	K02	Methyl ethyl ketone		7.77	4.4	2.5
A11	Cyclohexanol		8.50	2.0	6.6	K03	Methyl isobutyl ketone		7.49	3.0	2.0
A12	Ethylene glycol		8.25	5.4	12.7	K04	Methyl isoamyl ketone		7.80	2.8	2.0
A13	Propylene glycol		8.24	4.6	11.4	K05	Diisobutyl ketone		7.77	1.8	2.0
A14	1,3-Butanediol		8.10	4.9	10.5	K06	Isophorone		8.10	4.0	3.6
A15	Glycerol		8.46	5.9	14.3	K07	Acetophenone		8.55	4.2	1.8
A16	<i>m</i> -Cresol		8.82	2.5	6.3	K08	Cyclohexanone		8.65	4.1	2.5
A17	Diethylene glycol		7.86	7.2	10.0	K09	Mesityloxide		7.97	3.5	3.0
A18	Dipropylene glycol <sup>a</sup>		7.77	9.9	9.0	K10	Benzaldehyde		9.15	4.2	2.6
A19	Ethyl lactate		7.80	3.7	6.1	N01	Acetonitrile		7.50	8.8	3.0
A20	<i>n</i> -Butyl lactate		7.65	3.2	5.0	N02	Butyronitrile		7.50	6.1	2.5
A21	Diacetone alcohol		7.65	4.0	5.3	N03	Nitromethane		7.70	9.2	2.5
B01	Acetic acid <sup>a</sup>		7.1	3.9	6.6	N04	Nitroethane		7.80	7.6	2.2
B02	Formic acid <sup>a</sup>		7.0	5.8	8.1	N05	2-Nitropropane		7.90	5.9	2.0
B03	Butyric acid <sup>a</sup>		7.3	2.0	5.2	N06	Nitrobenzene		8.60	6.0	2.0
B04	Acetic anhydride		7.5	5.4	4.7	N07	Formamide		8.40	12.8	9.3
B05	Water <sup>a</sup>		6.0	15.3	16.7	N08	Dimethyl formamide		8.52	6.7	5.5
B06	Water-urea (satd.) <sup>a</sup>		8.8	13.0	15.2	N09	Aniline		9.53	2.5	5.0
C01	2-Methoxyethanol		7.9	4.5	8.0	N10	Ethanolamine		8.35	7.6	10.4
C02	2-Ethoxyethanol		7.85	4.5	7.0	N11	Dipropylamine		7.50	0.7	2.0
C03	2-Butoxyethanol		7.76	3.1	5.9	N12	Diethylamine		7.30	1.1	3.0
C04	2-Ethoxyethyl acetate		7.78	2.3	5.2	N13	Cyclohexylamine		8.45	1.5	3.2
C05	2-(2-methoxyethoxy)ethanol		7.90	3.8	6.2	N14	Pyridine		9.25	4.3	2.9
C06	2-(2-butoxyethoxy)ethanol		7.80	3.4	5.2	N15	Morpholine		9.20	2.4	4.5
C07	Dimethyl diethylene glycol		7.70	3.0	4.5	N16	Diethylenetriamine		8.15	6.5	7.0
E01	Ethyl acetate		7.44	2.6	4.5	N17	Benzonitrile		8.50	6.5	2.5
E02	<i>n</i> -Butyl acetate		7.67	1.8	3.1	N18	<i>n</i> -Methyl-2-pyrrolidone		8.75	6.0	3.5
E03	Isobutyl acetate		7.35	1.8	3.7	N19	2-Pyrrolidone		9.5	8.5	5.5
E04	Isoamyl acetate		7.45	1.5	3.4	N20	Dimethyl acetamide		8.2	5.6	5.0
E05	Isobutyl isobutyrate		7.38	1.4	2.9	N21	Tetramethyl urea		8.2	4.0	5.4
E06	Gamma-butyrolactone		9.26	8.1	3.6	N22	Ethylene cyanohydrin		8.4	9.2	8.6
E07	Propylene carbonate		9.83	8.8	2.0	N23	Hexamethyl phosphoramide		9.0	4.2	5.5
E08	Ethylene carbonate		9.50	10.6	2.5	P01	Trimethyl phosphate		8.2	7.8	5.0
F01	Diethyl ether		7.05	1.4	2.5	P02	Triethyl phosphate		8.2	5.6	4.5
F02	Furan		8.70	0.9	2.6	S01	Diethyl sulfide		8.25	1.5	1.0
F03	Tetrahydrofuran		8.22	2.8	3.9	S02	Carbon disulfide		9.97	0.0	0.0
F04	Dioxane <sup>a</sup>		9.30	0.9	3.6	S03	Dimethyl sulfoxide		9.00	8.0	5.0
F05	Methylal <sup>a</sup>		7.35	0.9	4.2	S04	Dimethyl sulfone		9.3	9.5	6.0
F06	Anisole <sup>a</sup>		8.7	2.0	3.3	Z01	Benzene		8.95	0.5	1.0
H01	Carbon tetrachloride		8.65	0.0	0.0	Z02	Toluene		8.82	0.7	1.0
H02	Chloroform		8.65	1.5	2.8	Z03	Xylene		8.65	0.5	1.5
H03	Methylene chloride		8.91	3.1	3.0	Z04	Ethylbenzene		8.70	0.3	0.7
H04	Ethylene chloride		9.20	2.6	2.0	Z05	Styrene		9.07	0.5	2.0
H05	1,1,1-Trichloroethane		8.25	2.1	1.0	Z06	Tetralin		9.35	1.0	1.4
H06	1-Chlorobutane		7.95	2.7	1.0	Z07	Hexane		7.24	0.0	0.0
						Z08	Cyclohexane		8.18	0.0	0.0

<sup>a</sup> Values uncertain.

been suggested. These include using contours (Crowley *et al.*, 1967) and making an additional assumption that all solvents have the same solubility parameter, so triangular coordinates can be used (Teas, 1968).

In practice, comparing solubility data of the good solvent or bad solvent type while looking at a model is the most rapid and satisfactory method to study a given situation. With a little experience one need only study tables of solubility to visualize an entire problem. Physical differences in two polymers can be quickly established, since it is obvious from the data in Table III, for example, that polyvinylpyrrolidone dissolves in more solvents of lower solubility parameter than dextran, and that, there-

fore, certain energy properties in these two polymers are different. The lower solubility parameters of the solvents showing differences in solubility give a more precise indication of the nature of differences existing in the two polymers.

The three-dimensional solubility parameter has been used to correlate data on many organic systems (Beerbower and Dickey, 1968; Hansen, 1967a, b, c, 1968; Hansen and Skaarup, 1967; Skaarup, 1968). Figure 2 includes some of these data to show solubility relations among SBR rubber, polystyrene, poly(vinyl acetate), poly(vinylidene fluoride) (PVF), and lignin (Bjorkman, 1956). These materials show a systematic tendency to

- 01 Poly(vinyl pyrrolidone), British Drug Houses
- 02 Dextran C, British Drug Houses
- 03 Urea, commercially available
- 04 Dried whole blood, Plastic Surgery Dept.,  
Danish State Hospital, Copenhagen
- 05 Blood serum, Danish State Serum Institute, Copenhagen
- 06 Zein, commercially available (corn)
- 07 Sucrose, commercially available
- 08 Psoriasis scales, Dermatological Dept.,  
Danish State Hospital, Copenhagen
- 11  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
- 12  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- 13  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
- 14  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- 15  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
- 16  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
- P1 Titanium dioxide, good pigment grade
- 17  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
- 18  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
- 19  $\text{NH}_4\text{NO}_3$
- 110  $\text{NaNO}_3$
- 111  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
- 112  $\text{NaNO}_2$

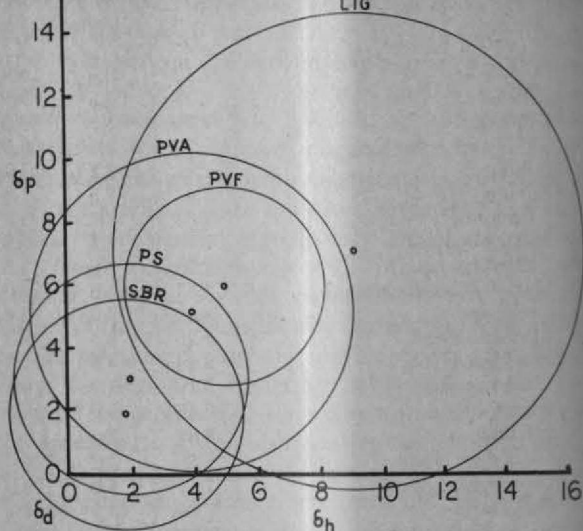


Figure 2. Regions of solubility for SBR rubber, polystyrene, poly(vinyl acetate), poly(vinylidene fluoride), and milled wood lignin

dissolve in solvents of increasingly higher solubility parameters. The general trend is for the volumes of solubility to be greater for a larger total solubility parameter. The crystallinity of PVF accounts for its relatively small volume. Polymers generally have high  $\delta_d$  components compared to the monomers used to make them. The swelling of elastomers has been studied in great detail, using the three-dimensional solubility parameter system, by Beerbower and Dickey (1968). These authors enlarged the number of solvents characterized and have correlated solubility parameters with other means to predict polymer-solvent interactions.

The  $\delta_p$  vs.  $\delta_h$  plot is generally the most useful single plot. The solubility region of urea is plotted in Figure 3 using these coordinates. The importance of the hydrogen bonding axis is immediately seen in this case, since urea dissolves in dimethylformamide (D), dimethyl sulfoxide (S), and the solvents having  $\delta_h$  higher than 6.0, except those in the low  $\delta_p$  and low  $\delta_h$  region occupied by cyclohexanol (C), and the simple alcohols greater in molecular weight than methanol (M). The usual symmetry of the volumes of solubility indicates an approximate center near  $\delta_d:\delta_p:\delta_h=12.0:10.5:13.5$ . A considerable and probably

Table III. Interaction of Various Solvents with Selected Organic Materials

Solvent	01	02	03	04	05	06	07	08	Solvent	01	02	03	04	05	06	07	08
A01	1		1			5		4	H01								2
A02	1		3			3		3-4	H02	2							2
A05	1							3-4	H03	3							2
A10	1							3	H04	4							2
A11	1		5					2	H07	5							1-2
A12	1	1	1	3	2	1	1	1	H08	4							2
A13	1		1			2		1-2	H09	5							1
A14	1		1					1-2	H10	5							1
A15	1	1	1	2	1		1	1-2	K01	3							3-4
A16	1		1	2	2	1		1	K03								3
A17	1		1		2	1		1-2	K06								2
A18	1		1					1-2	K07	3							1
A21	1							3	K08	5							2
B05	1	1	1	2	1		1	4	K10	1							1
B06	1	1		1	G <sup>a</sup>	1	1	1	N03	4							3
C01	1		1			1		3	N05	5							3
C02	1		1					3	N06	4							1
C03	1		5					3	N07	1	1	1	2-3	2	1	1	1
E01								3-4	N08	1		1			1	1	1-2
E02								3	N09	1		5			5		1
E06	1		5					2	N10	1	1	1	3	2	3	1	1
E07	2							2	S02								1
F01								4	S03	1	1	1		2	1	1	1
F03	5							3	Z1								1-2
F04	3							2	Z02								1-2
									Z06								1
									Z07								3-4

<sup>a</sup> Gel.

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