

PROCESS FOR PURIFICATION OF DIMETHYL SULPHOXIDE
(DMSO)

The present invention relates to a process
5 for the purification of dimethyl sulphoxide (DMSO) and
to the DMSO thus purified.

The DMSO currently available on the market is
a product which is already of a good purity. Its
commercial specifications are generally:

10	Purity	: ≥ 99.7 % by chromatography
	Acidity	: ≤ 0.04 mg KOH/g by potentiometry
	Crystallization point	: $\leq 18.1^{\circ}\text{C}$
	Visual appearance	: $\leq$ clear
15	Water content	: ≤ 0.15 %
	Colour (APHA)	: ≤ 10

French Patent Specification FR 2 014 385
describes a process for the preparation of purified
DMSO using an ion exchanger. In both examples of this
20 specification a highly basic resin of the Amberlite IR-
A 400 or Merck III type is employed to treat dimethyl
sulphide/DMSO/10% sulphuric acid ternary mixtures. In
fact, in this known process the purification seems to
be essentially brought about by a fractional
25 distillation of an aqueous solution of DMSO treated
beforehand with an anion exchanger.

Analyses of trace metals have now been
performed on a number of samples of commercial DMSO

from various sources. These analyses are reported in Table 1.

The sodium, iron, potassium, calcium, chromium, copper, nickel and zinc concentrations have been measured by ICP (plasma torch - atomic emission spectrometry, Perkin Elmer instrument, Optima 3000 model) and are expressed in ppb (1 ppb = 1 part by weight per thousand million = 1 μg per kg).

The list of the metallic elements which appears in Table 1 is not exhaustive in respect of the metallic elements present in these samples.

TABLE 1

Sample	Metal cations							
	Na	Fe	K	Ca	Cr	Cu	Ni	Zn
1	40	13	60	20	2	10	8	10
2	39	60	3	13	13	< 2	18	3
3	30	40	3	20	12	< 2	15	3
4	30	40	3	14	13	< 2	15	3
5	30	< 1	20	25	< 2	< 2	< 3	< 3
6	70	90	65	55	15	2	25	60
Detection limit	2	1	3	2	2	2	3	3

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For some applications, as for example in electronics or in pharmacy, the DMSOs analysed above

contain too many metallic impurities. In general, a DMSO containing less than 10 ppb of each alkali and alkaline-earth metal and metal contaminant would be necessary for most of the uses in the abovementioned
5 two technical fields.

The aim of the present invention is to find a process for purification of commercial DMSO which is already of a good purity, the latter being nevertheless insufficient for some applications.

10 Ion exchange by making use of resins is a technique widely employed for aqueous media and particularly allows deionized water to be obtained. Anion exchange in a liquid DMSO medium of low water content has already been carried out by Alan M. Phipps,
15 Anal. Chem. 40(12) pp. 1769-1773, 1968, for the purpose of measuring the quantities of anions bound to the resin in experimental conditions approaching thermodynamic equilibrium.

It has now been found that the use of a resin
20 in ammonium sulphonate form makes it possible, in DMSO of low water content or virtually anhydrous DMSO, to replace the metal cations M^{n+} (n having values from 1 to 4) with ammonium anions ($n \text{ NH}_4^+$).

According to one aspect of the present
25 invention, there is provided a process for purification of dimethyl sulphoxide to decrease its content of alkali metal, alkaline-earth metal and/or other metal cations, which process comprises placing the DMSO to be

purified in contact with a solid ion exchange resin of sulphonic type which has its active groups in ammonium sulphonate form (SO_3NH_4) and then separating from the solid the liquid purified DMSO with decreased content
5 of alkali metal, alkaline-earth metal and/or other metal cations, by any appropriate known means, especially filtration, percolation or centrifuging.

The purified DMSO obtained by the process according to the invention may thus have a very low
10 content of the metal cations.

A DMSO of low water content is advantageously treated, this content being preferably lower than or equal to 0.15 % by weight relative to the total weight.

The sulphonic type resin is preferably based
15 on a polystyrene-divinylbenzene copolymer. These resins have a backbone which stands up to chemical attacks and, in particular, they do not dissolve in DMSO. These resins are generally defined by their divinylbenzene content. In fact, the latter determines
20 the degree of crosslinking of the resin and hence the size of the pores in which the cation exchange takes place on the atomic scale.

The divinylbenzene in the copolymer preferably represents from 50 to 60 % by weight and the
25 polystyrene from 50 to 40 % by weight relative to the total weight of the copolymer, without taking the SO_3NH_4 groups into account. This divinylbenzene content

ensures a good kinetic activity of the exchange of the M^{n+} cations with $n \text{ NH}_4^+$.

The contact of the DMSO to be purified with the ion exchange resin is suitably brought about at a temperature ranging from 18.45°C (melting point of DMSO) to 120°C (thermal stability limit temperature of the resins). This temperature is advantageously between 19 and 80°C, preferably between 20 and 50°C.

To define the quality of the purified DMSO capable of being obtained by the process according to the invention, iron and sodium have been retained as tracer elements and indicators of the general content of alkali and alkaline-earth metal and metal cations.

According to another aspect, the present invention also provides purified DMSO characterized in that it has an Fe cation content lower than or equal to 1 ppb and an Na cation content lower than or equal to 2 ppb, the respective limits of detection of the analysis method using plasma torch - atomic emission spectrometry.

The invention is further illustrated with the reference to the following experimental part describing an example of embodiment of the present invention.

Experimental part

I. Analysis method:

ICP (plasma torch - atomic emission spectrometry) was employed for analysing the traces of

metals in the DMSO: the sample is introduced into a plasma torch, the various elements present are excited and emit photons whose energy is characteristic of the element, since it is defined by the electron structure of the element in question. A Perkin Elmer instrument (Optima 3000 DV model) was employed routinely.

II. Methodology:

Principle: the metal traces are in M^{n+} form. On passing the DMSO over a cation exchange resin, the latter itself in NH_4^+ form, the M^{n+} ions in solution are replaced with $n NH_4^+$.

III. Test:

Principle: with the aim of simplifying the analyses, sodium and iron were chosen as tracers representing all of the metallic impurities present in the DMSO.

Sodium is characteristic of atmospheric and accidental contamination (dust, environment) and iron is characteristic of contamination that can originate from the process (unit made of stainless steel).

DMSO doped with 1000 ppb of iron and 1000 ppb of sodium was placed in contact with a cation exchange resin in NH_4^+ form (2 g of resin per 100 g of DMSO) at 25°C. Samples of DMSO were taken in the course of time. The changes in the iron and sodium concentrations could thus be followed with time.

The resin employed was of the sulphonic type, supplied by the Purolite company under reference

MN 500. It is characterized especially by a divinylbenzene/styrene ratio of between 50/50 and 60/40. It was pretreated to obtain the H^+ form in the following manner: through 90 ml of resin placed in a column, 540 ml of 5% HCl are passed at a flow rate which is constant and such that the operation takes 30 to 45 minutes. The resin was then rinsed with deionized water until the water coming out was neutral. The resin thus obtained in H^+ form was next treated to obtain the NH_4^+ form in the following manner: over the 90 ml of resin placed in the column, 500 ml of an aqueous ammonia (NH_4OH) solution at a concentration of 2.5 % are passed at a flow rate which is constant and such that the operation takes 30 to 45 minutes. After having been rinsed with demineralized water until the water coming out was neutral, the resin was dried by suspension in methanol and evaporation under vacuum in the rotary evaporator (90°C, 2000 Pa) until a constant weight was observed.

Table 2 shows the change in the iron and sodium concentration in the DMSO as a function of time.

TABLE 2

Time (min)	0	5	10	20	45	60	90	120
[Na] (ppb)	980	120	50	21	10	6	< 2	< 2
[Fe] (ppb)	1020	350	150	70	25	15	6	< 1

CLAIMS

1. Process for purification of dimethyl sulphoxide (DMSO) to decrease its content of alkali metal, alkaline-earth metal and/or other metal cations, which process comprises placing the DMSO to be purified in contact with a solid ion exchange resin of sulphonic type which has its active groups in ammonium sulphonate form (SO_3NH_4) and then separating from the solid the liquid purified DMSO with decreased content of alkali metal, alkaline-earth metal and/or other metal cations.
2. Process according to Claim 1, in which a DMSO of low water content is treated.
3. Process according to claim 2 in which the water content of the DMSO is lower than or equal to 0.15 % by weight relative to the total weight.
4. Process according to any one of Claims 1 or 3, in which the resin is based on a polystyrene-divinylbenzene copolymer.
5. Process according to any one of Claims 1 to 4, in which the DMSO to be purified is contacted with the ion exchange resin at a temperature of 19 to 80°C.
6. Process according to Claim 5, in which the temperature is between 20 and 50°C.
7. Purified dimethyl sulphoxide obtained by the process according to any one of claims 1 to 6.



8. DMSO capable of being obtained by the process claimed in any one of Claims 1 to 6, which has an Fe cation content lower than or equal to 1 ppb and an Na cation content lower than or equal to 2 ppb, the
5 respective limits of detection of the analysis method using plasma torch - atomic emission spectrometry.